THE BIG CLEANUP

Bay of Quinte
Remedial Action Plan

Technical Report #17

MISA BATEA ASSESSMENT
FOR THE BAY OF QUINTE

Bay of Quinte RAP Coordinating Committee

February 1995

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BAY OF QUINTE

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PREFACE

This report has been prepared as part of the Bay of Quinte RAP under the auspices of the Canada-Ontario Great Lakes Remedial Action Plan program. Financial assistance and technical sponsorship for the investigations and research was provided by the Ontario Ministry of Environment and Energy, and Fisheries and Oceans Canada.

This report is the 17th in the Bay of Quinte RAP technical report series. It is part of the investigations, remedial action assessment and ecosystem monitoring conducted in support of the Bay of Quinte Remedial Action Plan. The report presents preliminary findings and data. The information presented does not necessarily represent the view or policies of the sponsoring agencies.

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ACKNOWLEDGEMENTS

EXECUTIVE SUMMARY

The mass balance model of toxic substances in the Bay of Quinte developed earlier by Drs. D. Mackay and M. Diamond of the University of Toronto, under contract to MOEE, has been updated with more recent field data, as well as MISA-BATEA pulp and paper discharge regulations. Their model is based on the fugacity/aquivalence concept (equivalent aqueous concentration), and predicts concentrations of inorganic and organic contaminants in Bay water, sediments, and several levels of biota up to the top predator (walleye). It produces results for five spatial segments of the Bay, including epilimnetic and hypolimnetic values in the deeper Middle and Lower Bays. Chemicals for which new data have become available are arsenic, cadmium, copper, zinc, pentachlorophenol (PCP), chloroform, 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF). In addition, model runs for lead (which was not previously considered) were done.

The only MISA-BATEA discharge regulation data available at this time is pulp and paper regulations for chloroform, TCDD, and TCDF. These numbers were used for the appropriate inputs; in addition, MISA monitoring regulation data for the pulp and paper sector were used for other chemicals as appropriate. New input data, collected in 1993 for the major tributaries and point source inputs as part of other programs, were also used. Atmospheric concentrations were available for 1992 from the Point Petre station and were input to the model. For several of the smaller inputs, no recent data were available and data from the 1988 RAP toxic contaminants study had to be used.

Model results have been compared with the Ministry's Provincial Water Quality Objectives (PWQO) and Provincial Sediment Quality Guidelines (PSQG), and, where appropriate, with sport fish contaminant guidelines. This comparison showed that predicted concentrations of all chemicals in water are within the PWQOs. Predicted PCP concentrations in fish are also within guidelines. However, predicted sediment metal concentrations exceed the PSQG Lowest Effect Level (LEL) values, and, occasionally (Cd and Pb in some segments), the Severe Effect Level (SEL) values. Predicted levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF are below some interim values which have been calculated for Thunder Bay; however, large uncertainties in the modelling of these compounds due to sensitivity to various model parameters as well as the value of the MISA-BATEA regulation detection limit, limit the accuracy of predictions of these

compounds.

Predicted concentrations of certain chemicals, especially cadmium, are higher than those of previous model results, despite reported decreases in point source and tributary loadings, as a result of updated information for atmospheric concentrations of these chemicals. It is believed that the more recent atmospheric data should accurately reflect this source of contamination. Examination of model results shows that atmospheric input accounts for about 10% or less of total input of heavy metals and PCP to the Upper Bay, but as much as 75% of input to the relatively shallow Hay Bay. Percentages are larger for atmospheric inputs of the other three organic chemicals to all bay segments.

Sensitivity tests have shown that model results for metals, chloroform and PCP in water are generally insensitive to values of most physical parameters. River flow, concentration of suspended particulates, sediment resuspension and burial are the most sensitive parameters for most metals. Chloroform is sensitive to solubility and vapor pressure, while PCP is sensitive to degradation rate. In sediments, deposition, resuspension and burial from the active layer tend to be important for most metals, while K_{ow} and sediment organic C are important for organics.

Model predictions would be improved by additional measurements for the above parameters; in addition, they would be improved by measurements of contaminants in Bay of Quinte water and inputs at lower detection levels. This should include other substances of concern such as PCBs, chlorinated pesticides, lower chlorinated phenols, agricultural chemicals such as atrazine, and other metals such as mercury and nickel. In addition, the fact that PWQOs are met but PSWGs are largely not met suggests that additional work on bioavailable fractions of both water and sediment contaminants is needed in order to more accurately set realistic objectives and assess their compliance.

MISA BATEA ASSESSMENT FOR THE BAY OF QUINTE

1.0   Introduction

In summer 1992, Drs. Don Mackay and Miriam Diamond completed the second report on modelling of toxic substances in the Bay of Quinte (Diamond, Mackay and Shiu, 1992). The report was an extension of the earlier toxics modelling study which they completed in 1991 on arsenic, pentachlorophenol and PCBs (Diamond and Mackay, 1991). The 1992 report included copper, zinc, cadmium, chloroform, trichloroethylene, naphthalene, benzo(a)pyrene, hexachlorobenzene, 2,3,7,8-TCDD, 2,3,7,8-TCDF, atrazine, dieldrin, mirex, and p,p'-DDT. These chemicals were modelled in water and sediment segments representative of the upper (west and east), middle and lower bays, and Hay Bay. A simplified food chain model was also used, including phyto- and zooplankton, benthos, forage fish, and small and large piscivores.

Loadings data used in the above study were generally obtained from results of the 1988 toxic contaminants study (Poulton, 1990). Since that time, the MISA monitoring regulations for the pulp and paper and municipal sectors have resulted in the acquisition of new data sets for the point source inputs. In addition, BATEA limits are being established as part of the draft MISA effluent limits regulations.

The purpose of this study is to use MISA BATEA limits (where established), and Monitoring Reg. data to update estimates of modelled toxic levels in the Bay of Quinte's water and sediments, and hence determine whether these limits will adequately protect the Bay of Quinte ecosystem, reduce the level of toxic contaminants in the bay, or restore the bay's beneficial water uses.

2.0 Overview of Model

The model is a multi-component version of the Quantitative Water-Air-Soil Interaction (QWASI) fugacity model developed by Mackay et al. (1983) and applied by Mackay (1989) to aquatic systems. The concept of fugacity as a surrogate for concentration in the modelling of organic contaminants in aqueous systems was introduced by Mackay and Patterson (1981). Its extension to aqueous systems involving non-volatile chemicals, i.e. the concept of "aquivalence", or "equivalent aqueous concentration", is discussed more fully elsewhere (Mackay and Diamond, 1989; Diamond and Mackay, 1991) and will be reviewed only briefly here.

Fugacity (f) expresses the escaping tendency of a chemical from any phase, and is linearly related to concentration through a capacity term, or Z value:

$$C = fZ \tag{1}$$

The ratio of Z values in two phases, Z_1/Z_2 is equivalent to a partition coefficient, K_{12}. The Z value for air, Z_A, is set to $1/RT$, where R is the gas constant and T the absolute temperature. Z values for other phases can be obtained by multiplying Z_A by the appropriate partition coefficients K_{ij} between the two phases of interest.

However, this formulation is inappropriate for nonvolatile chemicals such as metals as the air-water partition coefficient is zero in these cases. This results in the Z value for water, Z_W, becoming infinite, a clearly undesirable choice. Hence another equilibrium criterion must be established. As mentioned above, the concept of "aquivalence", is substituted. In this concept, calculations are based on the water phase, and Z_W is set to unity. This is equivalent to dividing the fugacity by the Henry's law constant (H) and multiplying the Z value by H. Thus equation (1) becomes

$$C = fZ = (f/H)(ZH) = QZ \tag{2}$$

where Q is the aquivalence. Since Z_W is defined as unity, Q in the water phase is simply the concentration in molar units. Likewise, Q in any other phase is expressed in molar units, and the Z values are dimensionless.

As with fugacity, at equilibrium the Q values for various phases are identical. For

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example, in a sediment-water system at equilibrium with the concentration C of contaminant at 1 mol/m^3, the aquivalence Q is also 1 mol/m^3. If the dimensionless sediment-water partition coefficient K_{SW} is 2000, then Z_W is 2000, and the contaminant concentration in sediment is 2000 mol/m^3. Similar relations exist for any other phase, such as fish, or even the atmosphere for volatile chemicals. Models written in terms of fugacity, aquivalence or concentration are equivalent algebraically.

The basic unit of the model is a well-mixed water column overlying a well-mixed bottom sediment layer as illustrated in figure 1. The processes treated and their rate expressions are listed in table 1. Rates of transport and transformation processes summarized in table 1 are expressed as the product of Q and a rate parameter D, which has units of flow (m^3/h), i.e. QD (mol/h). D values can be readily deduced for advective or diffusive flow, or reactions, by writing the conventional rate expression in concentration form and then replacing C by QZ and grouping all the terms except Q as the D value.

For each water and sediment segment a differential mass balance equation can be written as follows:

$$V_W Z_W dQ_W/dt = I + Q_S(D_3 + D_4) + Q_A(D_7 + D_8) + \sum Q_{Wi}D_I$$
$$- Q_W(D_4 + D_5 + D_6 + D_7 + D_0) \tag{3}$$
$$V_S Z_S dQ_S/dt = Q_W(D_4 + D_5) - Q_S(D_1 + D_2 + D_3 + D_4) \tag{4}$$

In these equations, V is volume (m^3), Z is the bulk phase aquivalence capacity (e.g. a volume-weighted combination of Z values for water and suspended particles or pore water and bottom sediment), Q is aquivalence, I is the chemical discharge or input to the water, and subscripts A, W, and S refer to air, water, and sediment, respectively. The term $\sum Q_{Wi}D_I$ is the sum of advective inflows from adjacent water compartments.

The steady-state solution to these equations is obtained when the derivatives are set to zero:

$$Q_W = [I + Q_A(D_7 + D_8) + \sum Q_{Wi}D_I] / [D_0 + D_6 + D_7 + (D_4 + D_5)(D_1 + D_2)/(D_1 + D_2 + D_3 + D_4)] \tag{5}$$

or $Q_W = [I + Q_A(D_7 + D_8) + \sum Q_{Wi}D_I] / D_T$ where D_T is the denominator above. (5a)

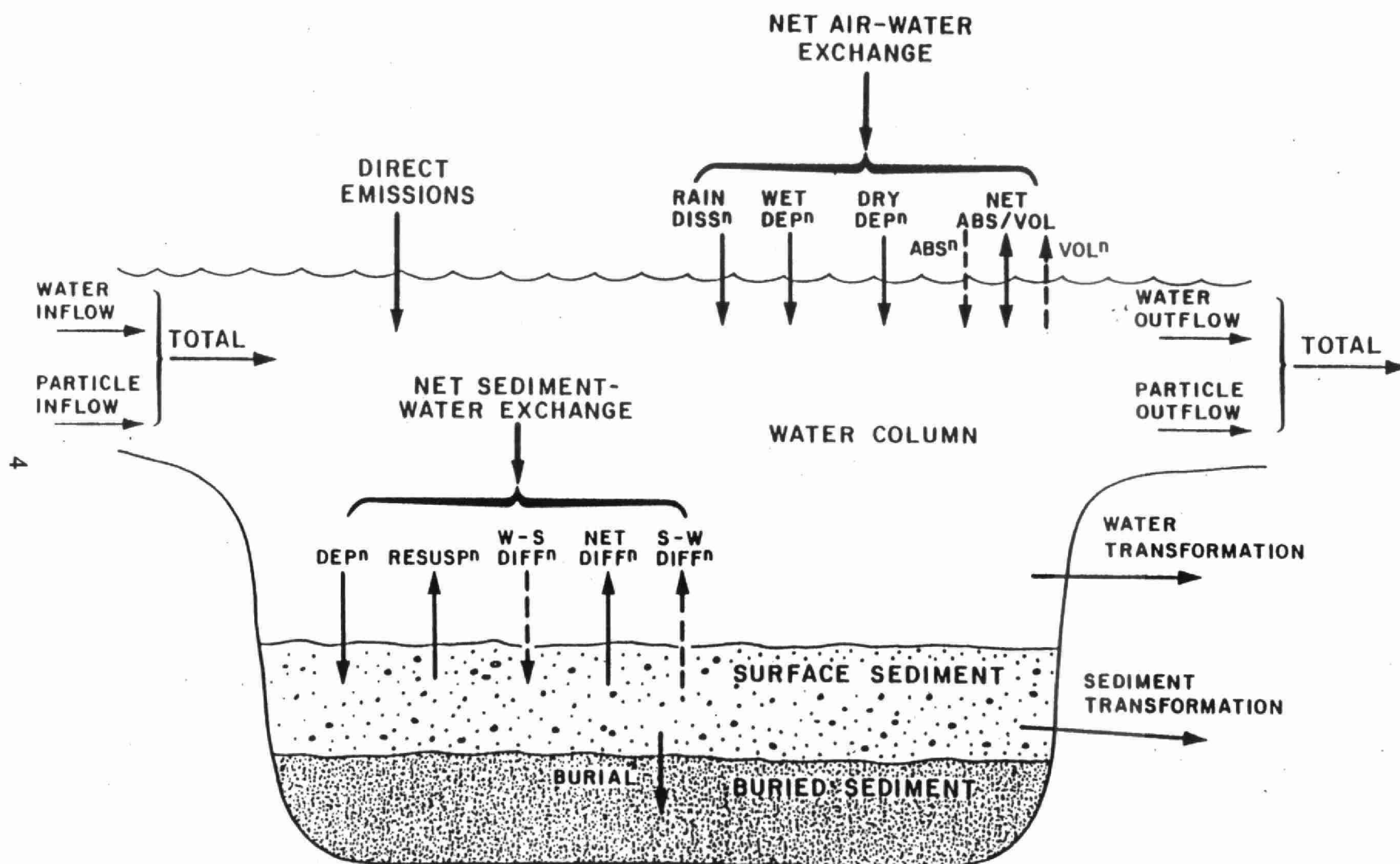and $Q_S = Q_W (D_4 + D_5)/(D_1 + D_2 + D_3 + D_4)$ (6)

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Figure 1. Illustration of the QWASI model.

Table 1. Definitions of transport and transformation D values and rate expressions.

Process	D Value	Rate Expressions (mol/h)
Sediment burial	D_1	GB.CS or (GB.ZS).QS or DB.QS
Sediment transformation	D_2	VS.CS.KS or (VS.ZS.KS).QS or DS.QS
Sediment resuspension	D_3	GR.CS or (GR.ZS).QS or DR.QS
Sediment to water diffusion	D_4	KT.AS.CS/KSW or (KT.AS.ZW).QS or DT.QS
Water to sediment diffusion	D_4	KT.AS.CW or (KT.AS.ZW).QW or DT.QW
Sediment deposition	D_5	GD.CP or (GD.ZP).QW or DD.QW
Water transformation	D_6	VW.CW.KW or (VW.ZW.KW).QW or DW.QW
Volatilization	D_7	KV.AW.CW or (KV.AW.ZW).QW or DV.QW
Air to Water Absorption	D_7	KV.AW.CA/KAW or (KV.AW.ZW).QA or DV.QA
Water outflow	D } D_0	GJ.CW or (GJ.ZW).QW or DJ.QW
Water particle outflow	D	GY.CP or (GY.ZP).QW or DY.QW
Rain dissolution	D_9 }	GM.CA/KAW or (GM.ZW).QA or DM.QA
Wet particle deposition	D_{10} } D_8	GC.CQ or (GC.ZQ).QA or DC.QA
Dry particle deposition	D_{11} }	GQ.CQ or (GQ.ZQ).QA or DQ.QA
Water inflow	D } D_I	GI.CI or (GI.ZW).QI or DI.QI
Water particle inflow	D	GX.CX or (GX.ZP).QI or DX.QI
Direct emissions	--	EW

Nomenclature and explanation:

The groups in parentheses are the D values (m^3/h), e.g., DB is (GB.ZS). The rate is the product of D and aquivalence Q, e.g., DB.QS.

G values are flows (m^3/h) of a phase, e.g., GB is m^3/h of sediment that is buried.

C values are concentrations (mol/m^3), the second letter being S sediment, W water, A air, Q aerosol, P water particles, I water inflow, X water particle inflow, J water outflow, and Y particle outflow.

QW, QS, QA, and QI are aquivalences (mol/m^3) of water, sediment, air, and water inflow.

Z values are aquivalence capacities (dimensionless), the second letter being defined as for concentration.

KS and KW are sediment and water transformation rate constants (h^{-1}).

KSW, e.g., ZS/ZW, is a sediment-water partition coefficient (dimensionless).

KAW, e.g., ZA/ZW, is an air-water partition coefficient (dimensionless).

KT is a sediment-water mass transfer coefficient and KV an overall (water-side) air-water mass transfer coefficient (m/h).

AW and AS are air-water and water-sediment areas (m^2).
VW and VS are water and sediment volumes (m^3).

The terms in the numerator of equation (5) are the inputs to the segment from discharges (I), the atmosphere $[Q_A(D_7 + D_8)]$, and from advective flow of particles and water from adjacent segments $\sum Q_{Wi}D_i$. The term D_T in the denominator is an overall loss D value from the water column and comprises outflow to other segments (D_0), transformation in the water column (D_6), evaporation (D_7), and net loss to the sediment, expressed as the transfer rate to the sediment ($D_4 + D_5$) multiplied by the fraction transformed or buried in deep sediments $(D_1 + D_2)/(D_1 + D_2 + D_3 + D_4)$.

For N pairs of water-sediment segments, N equations such as equation (5) exist, and solution is possible for the N unknown variables Q_W. The N sediment aquivalence values Q_S can then be deduced from versions of equation (6) and the entire set of concentrations, amounts, and process rates can be obtained. These equations are assembled in matrix form for computer solution.

Transfer between water layers in the vertical (e.g. epilimnion-hypolimnion) is similarly treated as advective-diffusive exchange between two adjacent water columns. The entire model consists of three water-sediment units (Upper West, Upper East and Hay Bay), and two epilimnion-hypolimnion-sediment units (Middle and Lower Bays) connected by water and particle movement (Figure 2). Further details of the solution method are given in Diamond and Mackay (1991).

The food chain model was developed independently of the Bay chemistry model, and treats six categories of biota (Figure 3). Phyto- and zooplankton reside in, and achieve, the same aquivalence as water. Benthos live in sediments and achieve the same aquivalence as the sediments. Benthivores (bottom-feeding fish such as sculpin) reside in the water and consume only benthos. Forage fish (e.g. young-of-the-year yellow perch) live in the water and are assumed to consume 75% plankton and 25% benthos. Small piscivores (<25 cm) (e.g. adult yellow perch) live in the water and consume a diet of 65% forage fish, 10% benthivores, 20% benthos and 5% plankton. Large piscivores (e.g. adult walleye) consume a diet of 80% small piscivores and 20% benthivores. For each of these consumer groups, a mass balance is computed, including uptake and clearance through the gills, consumption of food, and chemical loss by egestion and metabolism. Dilution of chemical by growth is also considered. At present, only organic chemicals are treated by the food chain model. Additional details of the solution are given in Diamond and Mackay (1991) and Clark et al. (1990).
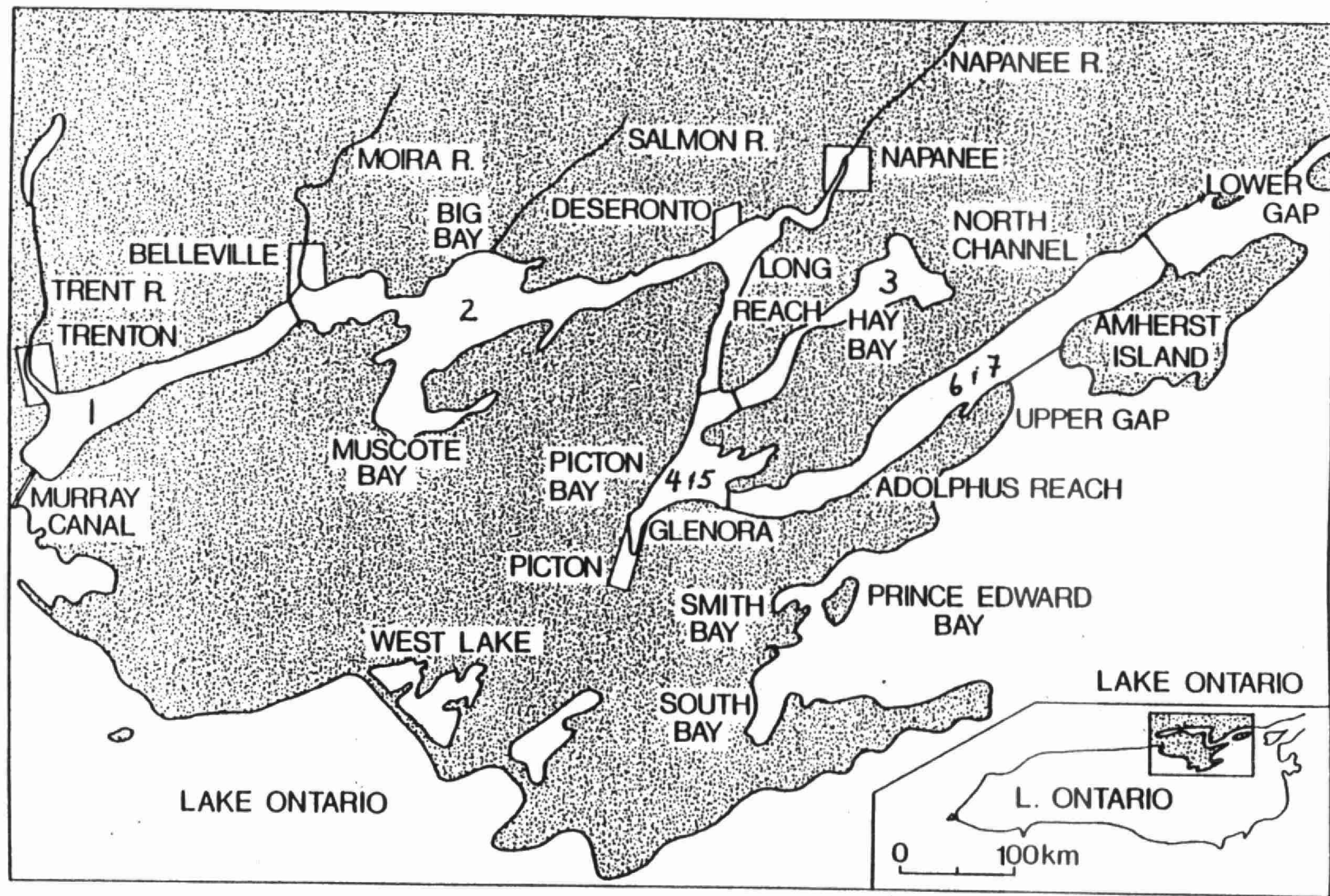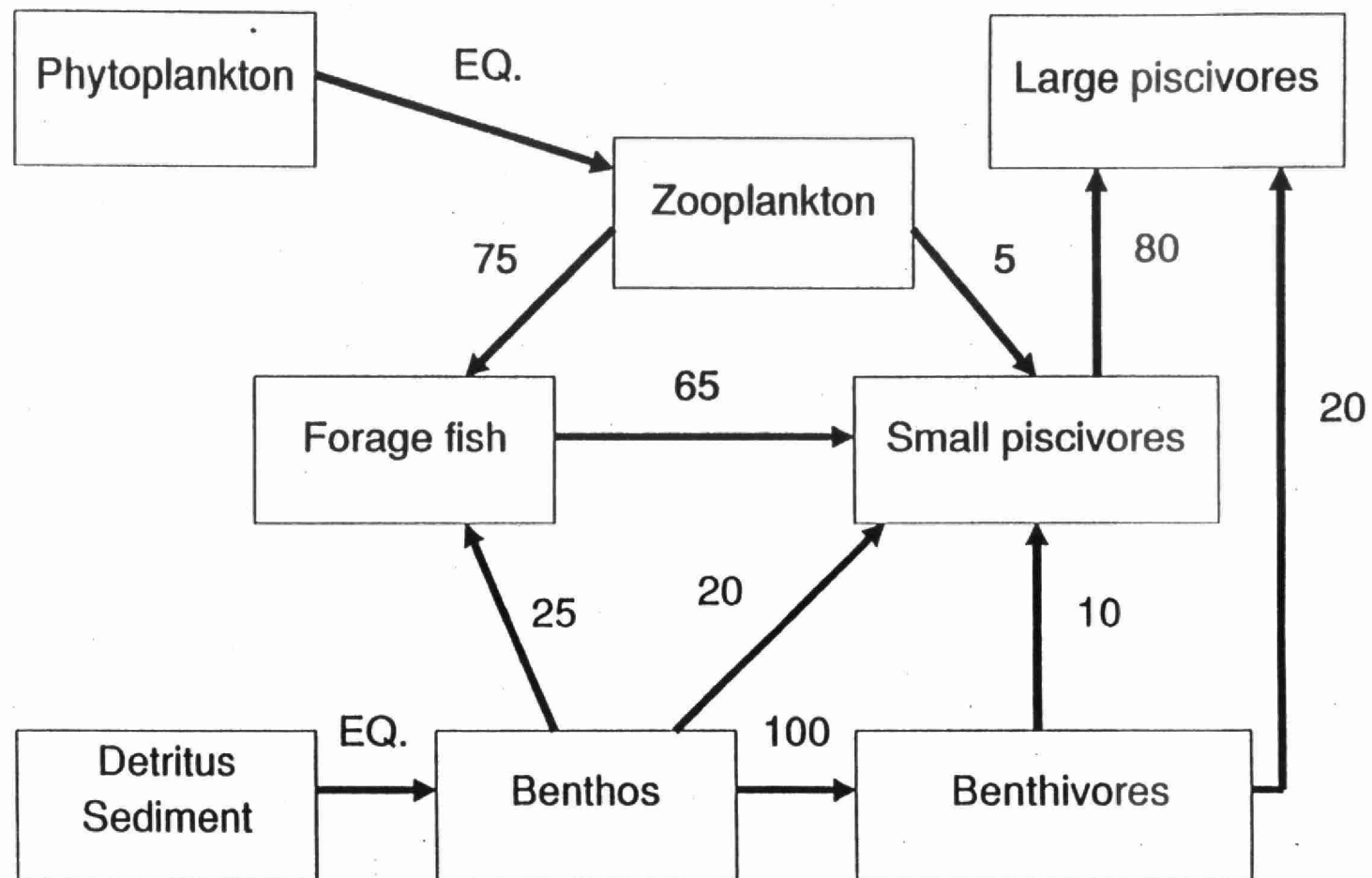
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Figure 2. Geographic segmentation used in the model of the Bay of Quinte.

Figure 3. Illustration of the food chain model.

3.0   Sources of Data

This project is designed to update the results of the earlier investigations using all data which have become available since 1988. In some cases, no more recent data were available and the data from the 1988 toxic contaminants survey (Poulton, 1990) had to be used. Active dischargers being considered include: Segment 1 (upper Bay west): Domtar Packaging, Domtar Wood Preserving, Sonoco (formerly Trent Valley Paperboard), Trenton STP, and CFB-Trenton STP. In Segment 2 (upper Bay east), there are Strathcona, and Bellevelle, Deseronto and Napanee STPs. Bakelite (reported in the 1988 survey) has ceased operation. In Segment 4 (middle Bay), only Picton STP is considered. The small STP at Prince Edward Heights is not considered; no data are available, and furthermore, it has been recommended that this plant be closed and the sewage diverted to Picton STP (RAP, 1993). The following presents an overview of the data used:

1.   The most comprehensive input concentration data for metal concentrations was the survey data collected by L. Wong of the Ministry's Biomonitoring Section, Environmental Monitoring and Reporting Branch, at Domtar Packaging, Sonoco, and Belleville and Trenton STPs between June and December, 1993. His concentration results are summarized in Table 2. Loadings derived from flow values provided by the sources to the Region, have been calculated on a monthly basis where possible, and tabulated in Table 3. For Trenton STP, June data were found to be considerably higher than those of other months, as well as the 1988 data (Poulton, 1990), and were ignored in calculation of averages. Many arsenic and cadmium values were below detection, as well as the occasional sample for other metals; one-half the detection limit was used in averaging.

2.   Effluent quality data for Domtar Wood Preserving in Trenton for July-September 1993 were obtained from MOEE-Southeastern Region. These included flow, heavy metals and chlorinated organics. Except for PCP, the latter were always below detection. Additional data for PCP were obtained from monthly Domtar reports as submitted to the MOEE Belleville district office. These results have also been included in Table 2, and the loadings derived therefrom in Table 3.3. Inputs from other sources, except Trenton CFB-STP, were obtained as averages of 1991-93 data from MOEE Southeastern Region. As these inputs have not been as well defined in recent years, the three-year average was used for these

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TABLE 2

HEAVY METAL CONCENTRATIONS AT BAY OF QUINTE INPUTS DURING 1993 (mg/L)

Source	Month	As	Cd	Cu	Pb	Zn	PCP(ug/L)
Domtar Wood	1						154.1
Preserv.	2						28.4
N. outfall	3						2.2
(09-02)	4						1.5
	5						0.5
	6						3.6
	7	ND	ND	0.0012	ND	0.0078	0.5
	8						0.5
	9	0.001	ND	0.0017	ND	0.018	55.4
	10						5.2
	11						92.1
	12						
	Av.	0.001	0.0000	0.0015	0.0000	0.0129	31.3
Domtar Wood	1						76.8
Preserv.	2						174.6
far north	3						22.7
outfall	4						102.9
	5						45.4
	6						48.1
	7	ND	ND	0.0037	ND	0.68	94.6
	8						380.8
	9	ND	0.0006	0.0042	0.008	0.17	21.7
	10						18.4
	11						21.4
	12						
	Av.		0.0003	0.0040	0.0040	0.4250	91.6
Domtar Pkg.	5	0.002	0.0033	0.073	0.003	0.270	0.10
(09-03)	7	0.002	0.0033	0.068	0.025	0.210	0.03
	8	0.002	0.0023	0.064	0.020	0.280	2.13
	9	0.003	0.0045	0.093	0.030	0.350	0.58
	12	0.002	0.0040	0.085	0.060	0.290	0.72
	Av	0.002	0.0035	0.077	0.028	0.280	0.71
Sonoco	7	0.001	0.0004	0.020	0.010	0.033	1.90
(09-11)	8	0.001	0.0004	0.014	0.013	0.041	2.04
	9	0.001	0.0004	0.015	0.010	0.038	0.89
	12	0.002	0.0001	0.008	0.007	0.057	1.97
	Av	0.001	0.0003	0.014	0.010	0.042	1.70
Belleville	6	0.005	0.0100	0.010	0.020	0.020	0.025
STP	8	0.001	0.0001	0.005	0.003	0.016	0.025
(03-02)	9	0.001	0.0001	0.023	0.012	0.017	0.025
	Av	0.002	0.0034	0.013	0.012	0.018	0.025
Trenton	6	0.005	0.0100	0.200	0.030	0.260	0.175
STP	8	0.001	0.0001	0.025	0.003	0.053	0.025
(03-01)	9	0.001	0.0003	0.031	0.003	0.038	0.025
	12	0.001	0.0001	0.037	0.016	0.130	0.190
	Av (Aug-Dec)	0.001	0.0002	0.031	0.007	0.074	0.080

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TABLE 3

HEAVY METAL LOADINGS AT BAY OF QUINTE INPUTS DURING 1993 (kg/d)

Source	Flow ($10^3m^3/d$)	Month	As	Cd	Cu	Pb	Zn	PCP(g/d)
Domtar Wood	0.978	1						150.71
Preserv.	0.146	2						4.15
N. outfall	0.682	3						1.50
(09-02)	0.946	4						1.42
	0.471	5						0.24
	0.516	6						1.86
	0.365	7	0	0	0.0004	0	0.0028	0.18
	0.279	8						0.14
	0.375	9	0.0004	0	0.0006	0	0.0068	20.78
	0.455	10						2.37
	0.459	11						42.27
		12						
	0.515636	Av.	0.0002	0.0000	0.0005	0.0000	0.0048	20.51
Domtar Wood	0.239	1						18.36
Preserv.	0.033	2						5.76
far N.	0.367	3						8.33
outfall	0.259	4						26.65
	0.088	5						4.00
	0.261	6						12.55
	0.136	7	0	0	0.0005	0	0.0925	12.87
	0.099	8						37.70
	1.083	9	0	0.00065	0.0045	0.0087	0.1841	23.50
	0.261	10						4.80
	0.131	11						2.80
		12						
	0.268818	Av.	0	0.0003	0.0025	0.0043	0.1383	14.30
Domtar Pkg.	4.257	5	0.0085	0.0140	0.311	0.011	1.149	0.43
(09-03)	4.578	7	0.0092	0.0151	0.311	0.114	0.961	0.11
	4.794	8	0.0096	0.0110	0.307	0.096	1.342	10.19
	4.685	9	0.0141	0.0211	0.436	0.141	1.640	2.72
	4.552	12	0.0091	0.0182	0.387	0.273	1.320	3.28
		Av	0.010	0.0159	0.350	0.127	1.283	3.34
Sonoco	1.892	7	0.0019	0.00076	0.038	0.019	0.062	3.59
(09-11)	2.096	8	0.0021	0.00084	0.029	0.027	0.086	4.28
	2.029	9	0.0020	0.00081	0.030	0.020	0.077	1.81
	2.299	12	0.0046	0.00023	0.018	0.016	0.131	4.53
		Av	0.0027	0.0007	0.029	0.021	0.089	3.55
Belleville	34.78	6	0.1739	0.3478	0.348	0.696	0.696	0.87
STP	23.21	8	0.0116	0.0023	0.121	0.058	0.371	0.58
(03-02)	26.2	9	0.0131	0.0026	0.603	0.314	0.445	0.66
		Av	0.066	0.0025*	0.357	0.356	0.504	0.70
Trenton	13.465	6	0.0673	0.1347	2.693	0.404	3.501	2.36
STP	9.979	8	0.0050	0.0010	0.249	0.025	0.529	0.25
(03-01)	10.535	9	0.0053	0.0032	0.327	0.026	0.400	0.26
	13.106	12	0.0066	0.0013	0.485	0.210	1.704	2.49
		Av (Aug-Dec)	0.0056	0.0018	0.354	0.087	0.878	1.00

* Questionable June value omitted

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data unless otherwise stated. For CFB-STP, the 1988 data (Poulton, 1990) were used, as these were the only available figures.

4. The only MISA control regulation that has so far appeared is that for the pulp and paper sector (MOEE, 1993). It contains compliance limits for TCDD, TCDF, and chloroform for Domtar Packaging, Sonoco and Strathcona Paper. Actual numerical loading values were given for chloroform; for TCDD and TCDF, the regulation says they should be non-measurable at the available regulation method detection limit (RMDL). (20 pg/L TCDD and 50 pg/L TCDF). As available laboratory data suggest that these compounds can be detected at levels of about 3 to 4 pg/L, I have used one-tenth of RMDL as concentrations to compute potential loadings.

5. For some additional parameters not included in the control regulation, MISA monitoring regulation data were used for the pulp and paper sector. Flow and pentachlorophenol (PCP) data were available for Domtar Wood Preserving, and flow data for Domtar Packaging, Sonoco, and Strathcona Paper for 1991-92. Data for several metals and chloroform were also obtained from MOEE Southeastern Region for Domtar Packaging. Average values were used in the analysis. It should be noted that flows for Sonoco in 1991-92 were considerably higher than those for the same source (as Trent Valley Paperboard) in 1988. The reason for this change is not known.

6. Tributary monitoring data were obtained from the MOEE Enhanced Tributary Monitoring Program (1991-93) for Trent, Moira, Salmon, and Napanee Rivers, and Picton Marsh Creek. These primarily included heavy metal concentrations. 1993 average concentrations are given in Table 4. Average flow data were obtained from Water Survey of Canada streamflow records. Data were also available for Demorestville and Sawguin Creeks but were not used as the inputs are small compared to other inputs into the Upper Bay East section of the model.

7. As part of the APIOS (Acidic Precipitation in Ontario Study), air samples are collected from an ambient monitoring network which includes one station in the Quinte area (Point Petre). Metals data are available for 13 samples at Point Petre in 1992 (MOEE, unpublished). Additional data are also available for 1990 (MOEE, 1994), and 1991 (MOEE, unpublished), including also a station at Campbellford which was discontinued after 1991. The data show some

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TABLE 4

TRIBUTARY CONCENTRATIONS OF HEAVY METALS OF INTEREST, 1993 (ug/L)

Location	# samples	As Median	% > D.L.	Cd Median	% > D.L.	Cu Median	% > D.L.	Pb Median	% > D.L.	Zn Median	% > D.L.
Upper Bay West											
Trent R.	45*	<1.0	14	<0.2	18	0.9	93	<5.0	2	1.7	100
Upper Bay East											
Moira R.	10**	4.0	100	<0.2	20	0.8	70	<5.0	0	2.3	100
Salmon R.	9***	<1.0	8	<0.2	11	<0.5	44	<5.0	11	2.8	100
Napanee R.	9***	<1.0	0	<0.2	0	1.0	100	<5.0	0	2.3	100
Consensus		3.0		<0.2		0.8		<5.0		2.4	
Middle Bay											
Picton Marsh Creek	5	<1.0	20	<0.2	0	1.9	100	<5.0	20	8.6	100

NOTE: All above data are from the MOEE Enhanced Tributary Monitoring Program
* 7 samples for As and Zn, 45 for all other metals.
** 17 samples for As, 10 samples for all other metals.
*** 12 samples for Cd, 9 for all other metals.

irregular and between-year variation. Being the most recent data, the 1992 data were used in the model (Table 5); however, the effect of variation of the atmospheric input is examined later in this report. Additional unpublished data for dry deposition of several organics at Point Petre in 1992 (M. Shackleton, STB, MOEE, pers. comm.) also showed irregular variations for the levels of several contaminants in air. These variations were not generally significant as ranges between minimum and maximum were usually high. Therefore, these values were averaged (Table 5).

8.   No new data were available for Trenton-CFB, Deseronto, Napanee or Picton STPs; consequently the 1988 data had to be used.

The extent of this project is limited by the availability of "real" data for most of the substances modelled by Mackay and Diamond. Many of the data points obtained from the above sources are below detection; for some chemicals where only a portion of the data are non-detect, one-half the detection limit was used for non-detects. This occurred mostly with arsenic, cadmium, TCDD, TCDF and PCP, and occasionally for copper and chloroform. For PCB, HCB, DDT, dieldrin, mirex and trichloroethylene, the limited amount of all data are virtually all non-detect; therefore, no attempt was made to model these compounds; likewise for naphthalene, benzo(a)pyrene and atrazine, few, if any, data were available. This restricted the present study to arsenic, cadmium, copper, lead, zinc, chloroform, TCDD, TCDF and PCP. It should be noted that lead was not considered by Mackay and Diamond; however, its accuracy is also limited by a large number of non-detects for which one-half the detection limit was used. In this context, it should be noted that statistical methods such as the maximum likelihood method (MLE) are available for estimating mean data when non-detects are present (e.g. El-Shaarawi, 1989); however, the quantity of "detected" data required for these methods was generally not present.

A summary of the input data used in the model (including averages taken from Tables 2-5) is given in Table 6. Pulp and paper sector MISA control regulation values as described above have been used for chloroform at Domtar Wood Preserving, Sonoco and Strathcona; the one-tenth of RMDL value has been used for TCDD and TCDF at all inputs as this is likely to be incorporated in other MISA control regulations. In addition, tributary concentrations for TCDD, TCDF and chloroform assumed by Diamond et al. (1991) have been retained, as well as tributary concentrations in segment 3 (Hay Bay) for other parameters. In general, these constitute a small fraction of input levels.

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TABLE 5

CONCENTRATIONS OF CONTAMINANTS IN AMBIENT AIR (ng/m^3)

Parameter	(assumed) Diamond et al. (1991, 1992)	(Campbellford and Pt. Petre) (1990-91) (MOEE, 1994)	(Pt.Petre) M. Shackleton (1992) (MOEE, unpublished)	(Dorset) N. Reid et al.
As	0.1	0.8	0.3	
Cd	0.5	0.29	0.12	
Cu	0.01	2.7	1.1	
Pb	-	9.0	1.6	4
Zn	0.1	12.9	3.2	
PCP	0.1	-	-	
PCBs	1	-	1.24 (1990), 0.706 (1991-92)	
HCB	8 - 24	-	0.123 (1990), 0.0041 (1991)	
chloro.	17000.	-	-	
TCDD	1.E-6	-	-	
TCDF	2.5E-6	-	-	

Note: Data from Mackay and Diamond are from a variety of sources cited in the report; in some cases, assumed (Cu, Zn) or "background" (As, PCP) values (Diamond and Mackay, 1991) with no reference provided were used.

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TABLE 6

SUMMARY OF INPUT DATA USED IN MISA-BATEA MODEL FOR BAY OF QUINTE (kg/d unless otherwise noted)

	Source	Arsenic	Cadmium	Copper	Lead	Zinc	TCDD	TCDF	chloroform	PCP
SEGMENT 1	Domtar WP, N. outfall	0.0002	0	0.0005	0	0.0048	8.0E-09	2.0E-08	0.416	0.0205
	Domtar WP. far N. outfall	0	0.0003	0.0025	0.0043	0.1383	5.4E-09	1.3E-08	NM	0.0143
	Domtar PKG.	0.01	0.0159	0.35	0.127	1.283	2.1E-08	6.4E-08	0.004 *	0.0033
	Sonoco	0.0027	0.0007	0.029	0.021	0.089	7.5E-09	1.9E-08	0.373	0.0036
	Trenton STP	0.0056	0.0018	0.354	0.087	0.878	2.6E-08	6.4E-08	0.035 *	0.001
	CFB-Trenton STP	0 *	0 *	0.0075 *	0 *	0.026 *	4.0E-09	1.0E-08	0.011 *	0.0002 *
	Total Load (kg/d)	0.0185	0.0187	0.7435	0.2393	2.4191	7.2E-08	1.9E-07	0.839	0.0429
	Trent R. Concn. (mg/L)	0.0005 #	0.0001 #	0.0009	0.0025 #	0.0017	5.0E-11 ##	1.0E-11 ##	0.00025 ##	4.3E-06 *
SEGMENT 2	Belleville STP	0.066	0.0025	0.357	0.356	0.504	6.0E-08	1.5E-07	0.144	0.0007
	Deseronto STP	0 *	0 *	0.016 *	0 *	0.027 *	2.8E-09	7.0E-09	0.002	0.00007 *
	Napanee STP	0 *	0 *	0.058 *	0 *	0.175 *	1.2E-08	3.1E-08	0.006	0.0005 *
	Strathcona	NM	NM	0.011 **	0.005 **	0.046 **	6.6E-09	1.7E-08	0.237	NM
	Total Load (kg/d)	0.066	0.0025	0.442	0.361	0.752	8.1E-08	2.0E-07	0.389	0.00127
	Consensus of trib. concns. (mg/L) ***	0.003	0.0001 #	0.0008	0.0025 #	0.0024	5.0E-11 ##	1.0E-11 ##	0.00025 ##	7.0E-07
SEGMENT 4	Picton STP (kg/d)	0 *	0 *	0.024 *	0 *	0.046 *	6.8E-09	1.7E-08	0.017	0 *
	Trib. concn. (mg/L) (Picton Marsh Creek)	0.0005 #	0.0001 #	0.0019	0.0025 #	0.0086	5.0E-11 ##	1.0E-11 ##	0.0013 ##	0 *
ATMOSPHERIC (All segments) (concn. in ng/m^3)		0.3 **	0.12 **	1.1 **	1.6 **	3.2 **	1.0E-06	2.5E-06	17000	0.1

NOTE: Sources of above data are described in the text, and are generally 1993 data (with exceptions described).
        MISA effluent regulation loads have been used for TCDD, TCDF and chloroform where possible as described in the text.
        * - 1988 data
        ** - 1990 data (1992 for air)
        *** - Approximate flow-weighted average of three input streams (see Table 4)
        NM - not measured (assumed to be zero)
        # - Values below detection. 1/2 detection limit assumed.
        ## - Assumed values from Diamond et al. (1992)

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4.0 RESULTS

Model simulations of best updated conditions described above (including BATEA treatment technology for chloroform, TCDD and TCDF as described in the MISA pulp and paper discharge regulation) are presented in Tables 7 and 8, and Figures 4 to 21. In Table 7, results of simulations of 1988 data for water in several representative model segments (Diamond, Mackay and Shiu, 1992) are compared with the more recent data. Table 8 presents similar results for sediments. Differences between the two years' simulations are discussed in the text.

It should be recalled that for cadmium and the organics, many of the input data were below detection limits, both in 1988 as used by Diamond et al. (1992) and in the present study. Diamond et al. (1992) had to back-calculate the concentration of some inputs from fish data, which was the only detected concentration for some of the organic compounds. Attempts at back-calculations could have been improved, had more recent fish data been available. However, no more recent fish samples from the Bay of Quinte have been analyzed for these contaminants (M. Whittle, Department of Fisheries and Oceans, pers. comm.). Some of the approximations used were indicated in Table 6 and discussed in section 3.0.

4.1 Arsenic

Arsenic concentrations in the various media are given in Figure 4, while inputs and intersegment movements are given in Figure 5. Reduced concentrations of arsenic in the Trent and Moira Rivers more than compensate for an increase in point source (Belleville STP) loadings in segment 2, as well as updated atmospheric arsenic concentrations (which are increased from Diamond et al's estimates). The effect of the latter can be seen in the data for Hay Bay, where there are no point sources and tributary inputs (Wilton Creek) are minimal. The net result is a decrease in water and sediment arsenic concentrations (Figure 4). All water concentrations remain below the Provincial Water Quality Objective (PWQO) value of 100 μg/L; however, segments 2 to 7 sediment arsenic levels are above the Lowest Effect Level (LEL) of the Provincial Sediment Quality Guidelines (PSQG) (6 μg/g). As stated by Diamond et al.

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TABLE 7

MODEL ESTIMATES OF CONTAMINANT CONCENTRATIONS IN BAY OF QUINTE WATER

Parameter	Segment 1 (Upper Bay West)		Segment 2 (Upper Bay East)		Segment 3 (Hay Bay)		Segment 6 (Lower Bay Epilimnion)	
(a) metals (ug/L)	M&D	Present	M&D	Present	M&D	Present	M&D	Present
As	0.658	0.183	1.441	0.883	0.574	0.577	0.819	0.631
Cd*	0.044	0.091	0.061	0.085	0.068	0.044	0.035	0.034
Cu	2.67	0.97	2.82	0.99	1.47	0.65	1.60	0.98
Pb	-	2.15	-	1.99	-	0.69	-	0.47
Zn	2.07	1.83	1.89	1.94	0.77	1.26	0.86	0.94
(b) organics (ng/L)								
Chloroform	222	229	174	178	106	107	96.1	97.9
Pentachlorophenol	4.69	0.77	0.52	0.084	3.8E-03	3.4E-03	9.7E-03	1.9E-03
2378-TCDD	4.3E-05	4.6E-05	3.9E-05	4.2E-05	1.1E-05	1.1E-05	1.9E-05	2.0E-05
2378-TCDF	3.1E-05	4.1E-05	4.8E-05	6.0E-05	3.3E-05	5.4E-05	2.7E-05	3.2E-05

Note: "M&D" refers to modelled results of Mackay and Diamond, using 1988 input data, with exception at *.
"Present" refers to present updated model results, using inputs described in section 2 of the text.
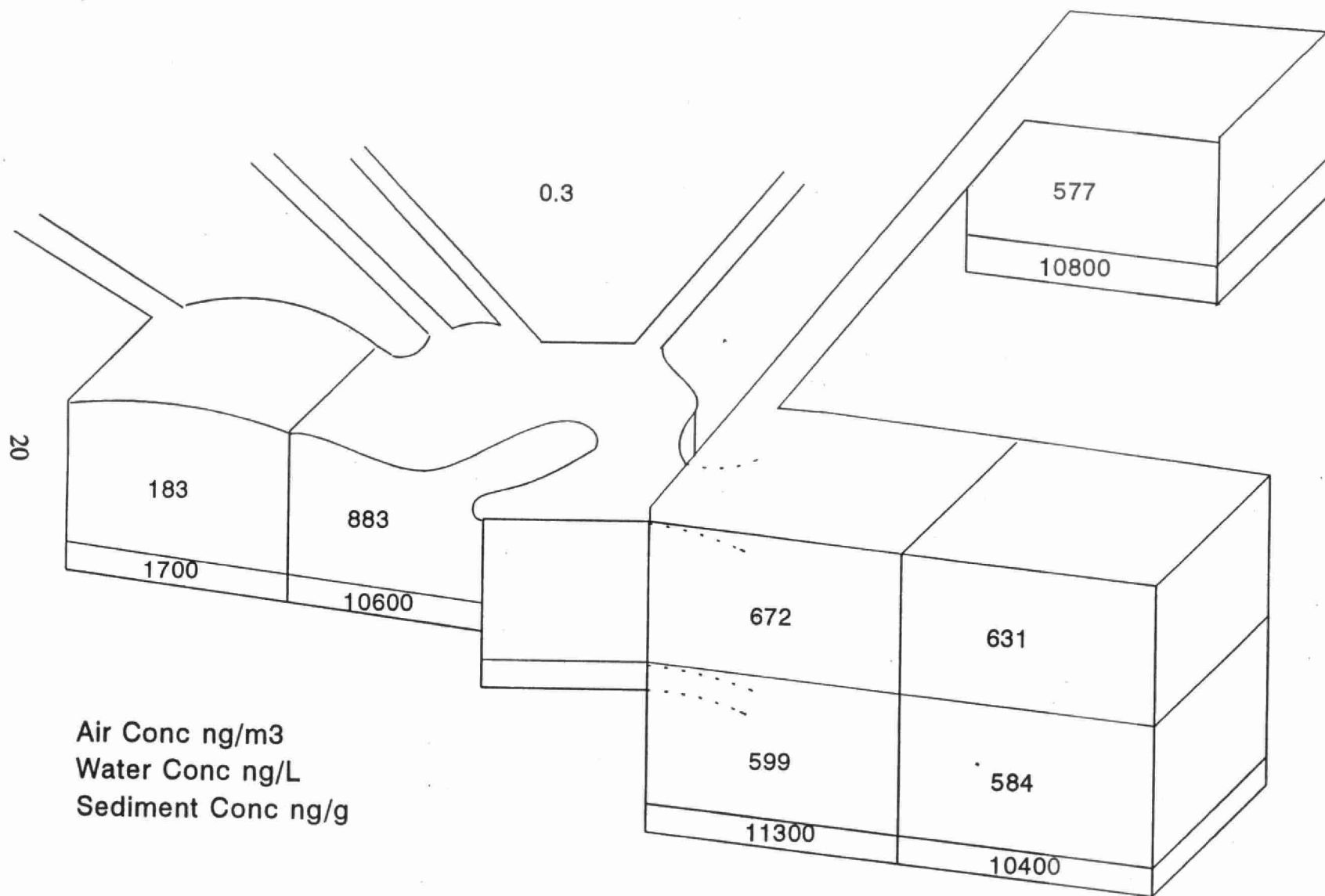* Recalculated with air [Cd] = 0.5 mg/m^3

TABLE 8

MODEL ESTIMATES OF CONTAMINANT CONCENTRATIONS IN BAY OF QUINTE SEDIMENTS

Parameter	Segment 1 (Upper Bay West)		Segment 2 (Upper Bay East)		Segment 3 (Hay Bay)		Segment 7 (Lower Bay)	
(a) metals (ug/g)	M&D	Present	M&D	Present	M&D	Present	M&D	Present
As	5.93	1.70	17.36	10.60	10.8	10.8	11.3	10.4
Cd*	3.53	7.25	6.94	9.70	18.1	11.5	27.6	28.1
Cu	46	17	65	23	62	28	55	46
Pb	-	198	-	258	-	252	-	571
Zn	109	96	140	144	135	219	220	232
(b) organics (ng/g)								
Chloroform	1.09	1.12	0.79	0.81	0.32	0.32	0.12	0.12
Pentachlorophenol	1.35	0.22	0.15	0.024	6.8E-04	6.0E-04	5.5E-04	5.2E-04
2378-TCDD	3.8E-03	4.0E-03	4.9E-03	5.3E-03	1.8E-02	2.9E-03	2.8E-02	2.9E-02
2378-TCDF	1.7E-03	2.3E-03	3.9E-03	4.9E-03	8.6E-03	8.7E-03	7.2E-03	8.5E-03

Note: "M&D" refers to modelled results of Mackay and Diamond, using 1988 input data, with exception at *.
"Present" refers to present updated model results, using inputs described in section 2 of the text.
* Recalculated with air [Cd] = 0.5 mg/m^3.

0.3

577

10800

20

183

883

1700

10600

672

631

Air Conc ng/m3
Water Conc ng/L
Sediment Conc ng/g

599

584

11300

10400

Figure 4: Updated conditions, arsenic concentrations
in water and sediment.
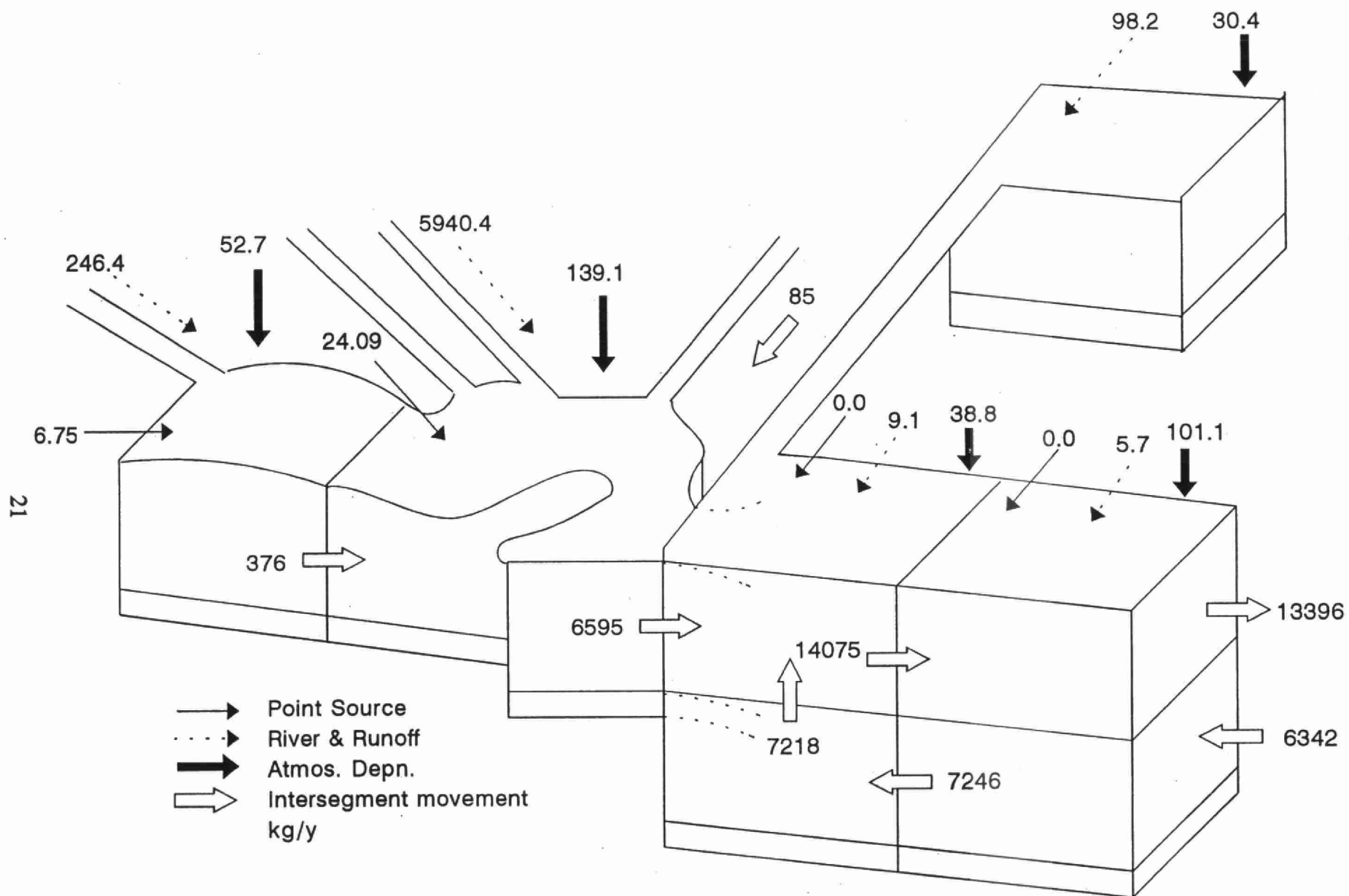
Figure 5: Updated conditions, estimates of loadings and chemical movement for arsenic.

(1992), upstream sources of arsenic on the Moira River must be controlled, for sediment values to decline below the LEL.

Spatial variation in sediment concentrations does not agree well with observed values. In Upper Bay west (segment 1), the modelled sediment concentration is 1.7 μg/g, which is less than observed values (Poulton, 1990) by a factor of about 3. But in Hay Bay, the modelled concentration is 10.8 μg/g, a value similar to those predicted for all segments but Upper Bay west. This result is about double the observed value (4.8 μg/g). Observed Middle Bay sediment concentrations are 10 to 19 μg/g, and 7 to 22 μg/g in the Lower Bay, in reasonable agreement with predictions. Doubling the sediment burial rate (assumed to be 0.275 g/m^2/d, Diamond and Mackay, 1991) decreased the sediment concentration only slightly to 8.8 μg/g. The values of atmospheric and tributary input also influence both water and sediment concentrations in this segment; improved data are required for both these items in order to improve model agreement. They are also affected by physical parameters such as partition coefficients and sedimentation and burial rates, which are not well known.

4.2 Cadmium

Cadmium concentrations in the various media are given in Figure 6, while inputs and intersegment movements are given in Figure 7. Estimation of cadmium levels entails problems due to "non-detects" in tributaries and many inputs; hence, approximations were required and the results can be regarded as only a first approximation.

The atmospheric concentration of cadmium in 1990-91 averaged 0.29 ng/m^3 (MOEE, 1994), and in 1992, 0.12 ng/m^3 (MOEE, unpublished). While Diamond et al. (1992) originally estimated an atmospheric level of 0.001 ng/m^3, this was revised in later calculations to 0.5 ng/m^3 (Strachan and Eisenrich, 1988; Diamond et al., to be published). The revision results in an approximate doubling of epilimnetic water cadmium concentrations, based on the assumed data used by Diamond et al (1992). Due to the non-detects found in the 1988 survey (Poulton, 1990); Diamond et al. used a unit loading into segment 1 and assumed tributary concentrations of 30 ng/L. These were "back-calculated from sediment concentrations", but the estimated sediment concentrations were higher than 1988 observed sediment data by factors of 2 to over 10. Concentrations in all segments were found to be quite sensitive to the atmospheric level used; the 500-fold change in atmospheric concentration resulted

22

23

0.12

43.5

11500

90.6

84.8

7250

9700

62.7

34.2

88.6

78.1

20900

28100
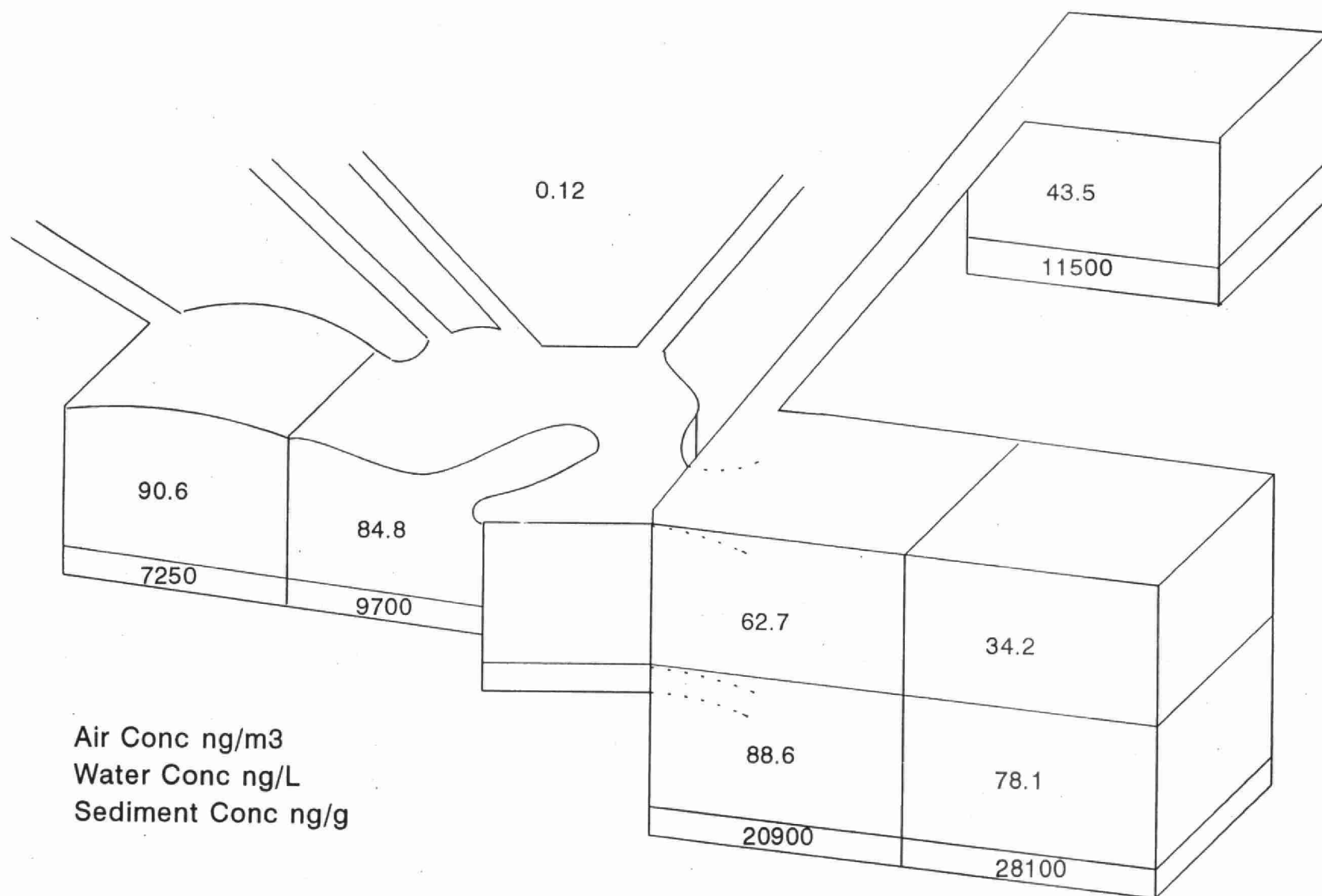
Air Conc ng/m3
Water Conc ng/L
Sediment Conc ng/g

Figure 6: Updated conditions, cadmium concentrations
in water and sediment.
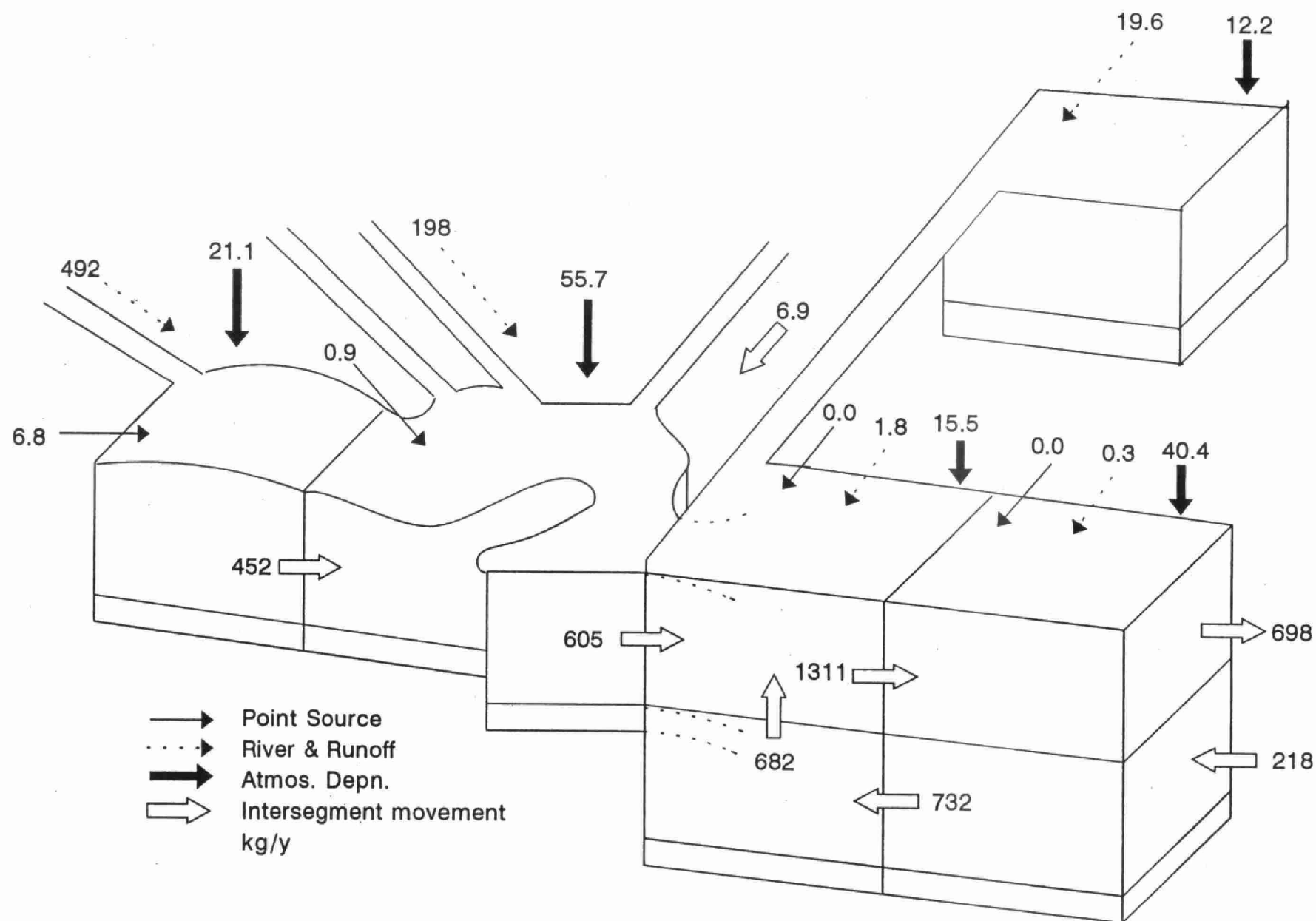
Figure 7: Updated conditions, estimates of loadings and chemical movement for cadmium.

Legend:
- → Point Source
- ·····▶ River & Runoff
- ➡ (filled) Atmos. Depn.
- ⇨ (outline) Intersegment movement

kg/y

Values shown in diagram:
19.6 12.2
198 492 21.1 55.7
0.9 6.9
6.8
0.0 1.8 15.5 0.0 0.3 40.4
452 605 1311 698
682 732 218

24

in sediment concentrations that were higher by factors of 1.7 to over 10, compared to Diamond's original calculation.

In 1993, source cadmium was generally detected at trace levels only from Domtar Packaging; the STPs indicated detectable (but questionable) concentrations only in June (plus a trace at Trenton in September) (Table 3). Modelled cadmium concentrations in water (figure 6, Table 7) were considerably below the detection limit of 0.2 μg/L; in sediments, the modelled results were higher than observed (Poulton, 1990) results by a factor of about 3 (Upper Bay West) to over 10 (Middle and Lower Bays) and over 20 (Hay Bay). Perhaps the Lake Ontario value of 24 ng/L (dissolved Cd, Rossmann and Barres, 1988) was an overestimate as evidenced by the high hypolimnetic and sediment results in the Lower Bay (segment 7). In addition, as with arsenic, the value of the burial rate in Hay Bay could be suspect; doubling this rate had a greater effect than with arsenic, causing a decrease of about 42%. At any rate, the model results indicate the need for improved input data at lower detection limits, both for tributaries and point sources. Due to the uncertainties described above in model inputs, comparison of results with objectives and guidelines is meaningless.

4.3 Copper

Copper concentrations in the various media are given in Figure 8, while inputs and intersegment movements are given in Figure 9. Increased atmospheric input (due to the availability of MOEE atmospheric data) was more than compensated by decreased point source and tributary inputs as determined by 1993 measurements (see input descriptions given earlier). The result is a rather uniform concentration of about 1 μg/L in the water and sediment concentrations that vary from 17 μg/g in Upper Bay West to 47 μg/g in Middle Bay. These are similar to 1988 observed concentrations in Middle Bay but lower than observed in Upper Bay. In the Upper Bay, river and runoff inputs dominate, while in the Lower Bay, exchange with Lake Ontario predominates over external inputs. Water concentrations are well below the PWQO of 5 μg/L. Maximum modelled sediment concentrations are higher than the LEL of 16 μg/g by a factor of almost 3, however further reductions in sediment copper levels will be difficult to achieve as the main controls come from outside the basin (tributaries and Lake Ontario).

25

648

27500

1.1

966

16700

988

22800

1060

982

1210

1180

47100

46300

Air Conc ng/m3
Water Conc ng/L
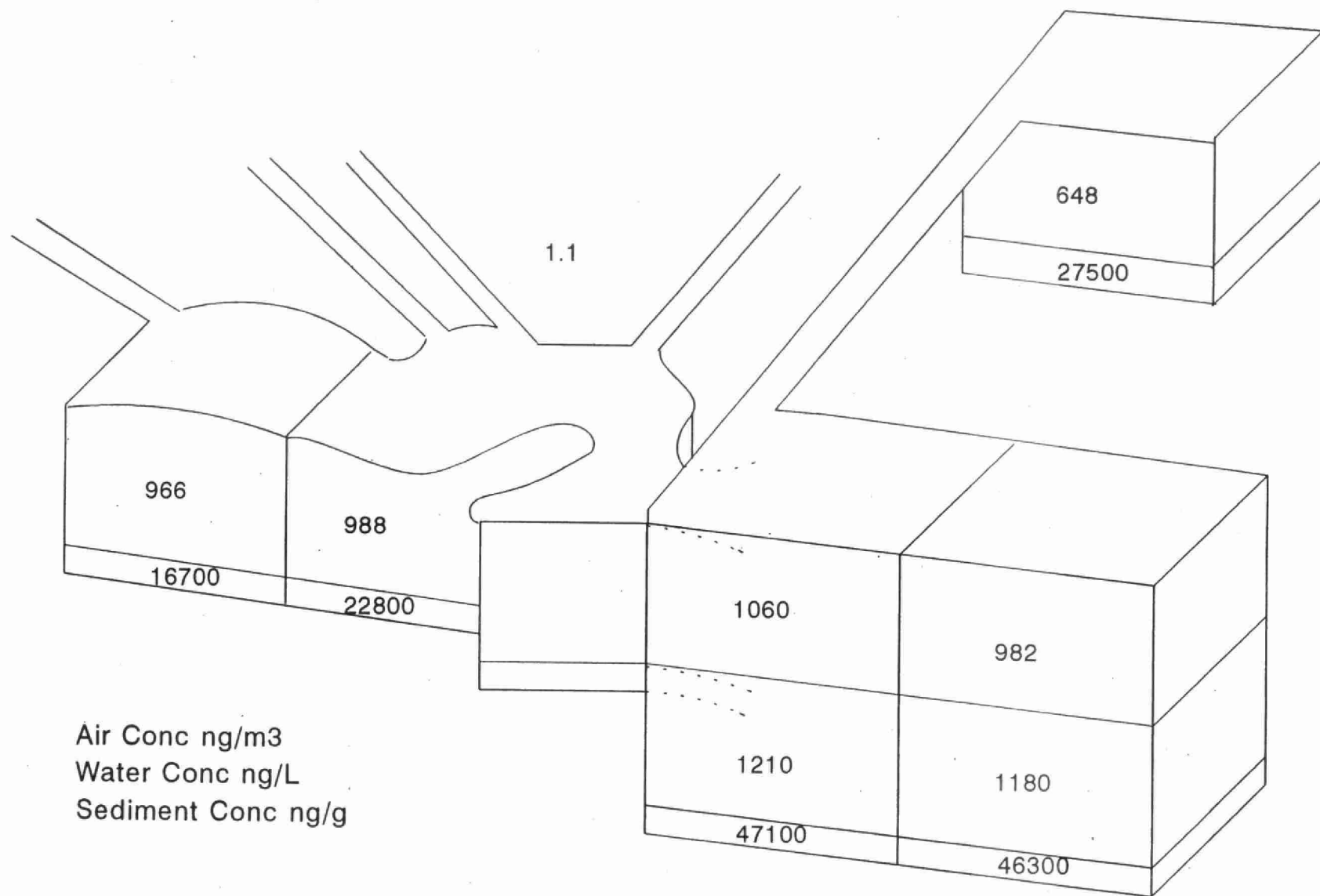Sediment Conc ng/g

26

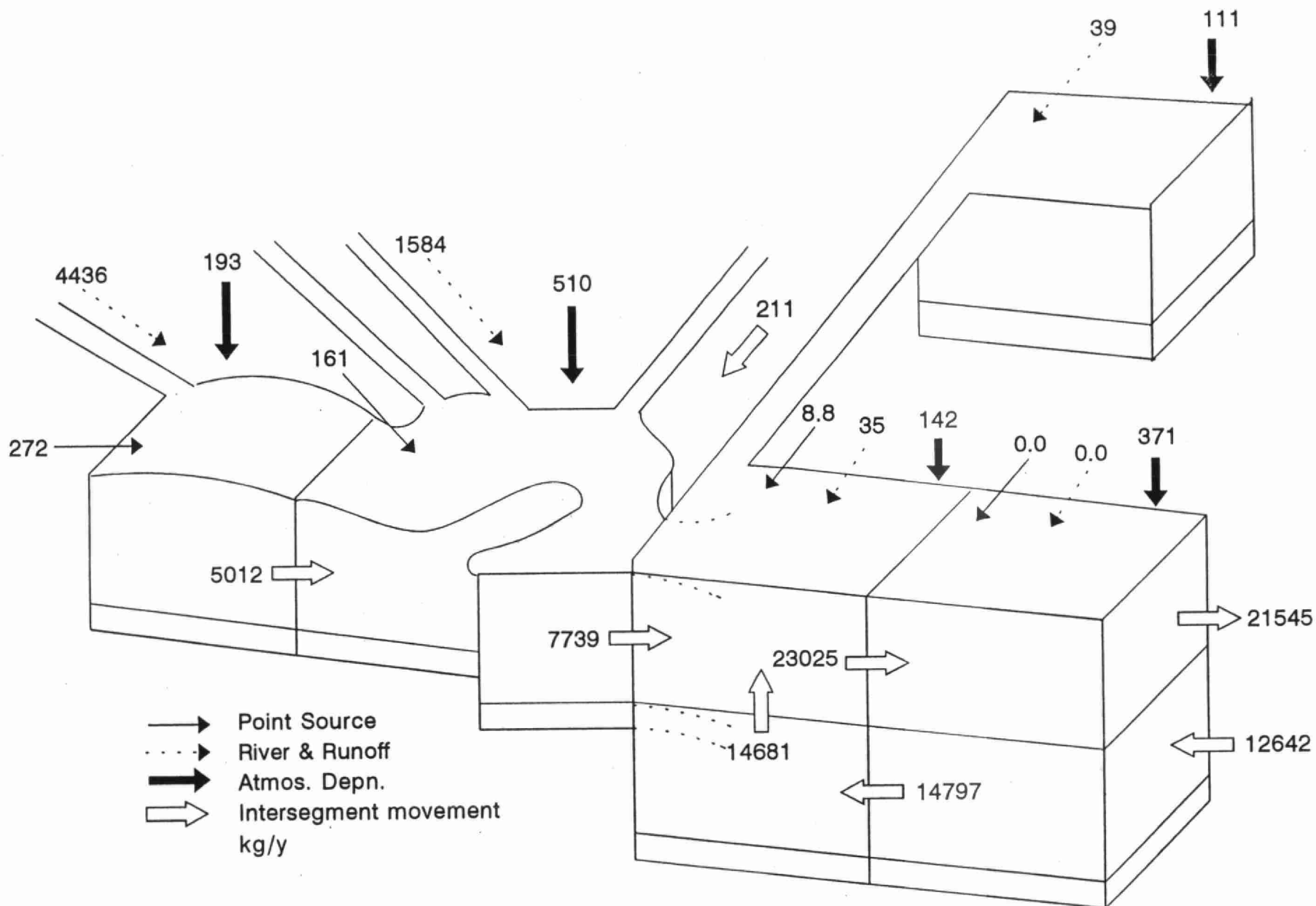Figure 8: Updated conditions, copper concentrations in water and sediment.

Figure 9: Updated conditions, estimates of loadings and chemical movement for copper.

4.4   Lead

Lead concentrations in the various media are given in Figure 10, while inputs and intersegment movements are given in Figure 11. The major input source to the Upper Bay is the Trent River, while atmospheric input predominates as an external source in the Middle and Lower Bays; it is, however, lower than the throughput of lead from upper reaches of the Bay except for Hay Bay. Throughput is, in fact, so important, that output from the Lower Bay hypolimnion (segment 7) is greater than input from the lake.

Lead has not been modelled previously in the Bay of Quinte. Only 5% of lead values in water were above the detection limit of 5 μg/L in the 1988 survey (Poulton, 1990); modelled values support this as they range from 2 μg/L to less than 0.5 μg/L. Modelled sediment Pb values range from 200 to 600 μg/g, and are far higher than measured 1988 values, which averaged 80 μg/g for the main portion of the bay. As this is a "first cut", some adjustment of partition coefficients may be undertaken.

4.5   Zinc

Zinc concentrations in the various media are given in Figure 12, while inputs and intersegment movements are given in Figure 13. In all segments except Upper Bay West, zinc concentrations have increased as a result of the increased value for atmospheric input (like several other parameters, Diamond's figure was just an estimate due to lack of data). Atmospheric input dominates local sources in Middle and Lower Bays, although downstream transport from Upper Bay is the predominant zinc source to Middle and Lower Bays. Exchange with Lake Ontario allows dilution of zinc concentrations in Lower Bay. Point source and tributary inputs are approximately the same as in 1988. While water concentrations are well below the PWQO of 30 μg/L, sediment concentrations exceed the LEL of 120 μg/g in all segments but Upper Bay West. Except in Hay Bay, water and sediment concentrations are similar to 1988 observed values (Poulton, 1990). Doubling the burial rate in Hay Bay (as tried with arsenic) reduces the sediment concentration in Hay Bay to a value less than that of Middle and Lower Bays, but still greater than the observed 1988 value. As with arsenic, better characterization of atmospheric and tributary inputs is required.

28

1.6

690

252000

2150

1910

198000

258000

Air Conc ng/m3
Water Conc ng/L
Sediment Conc ng/g

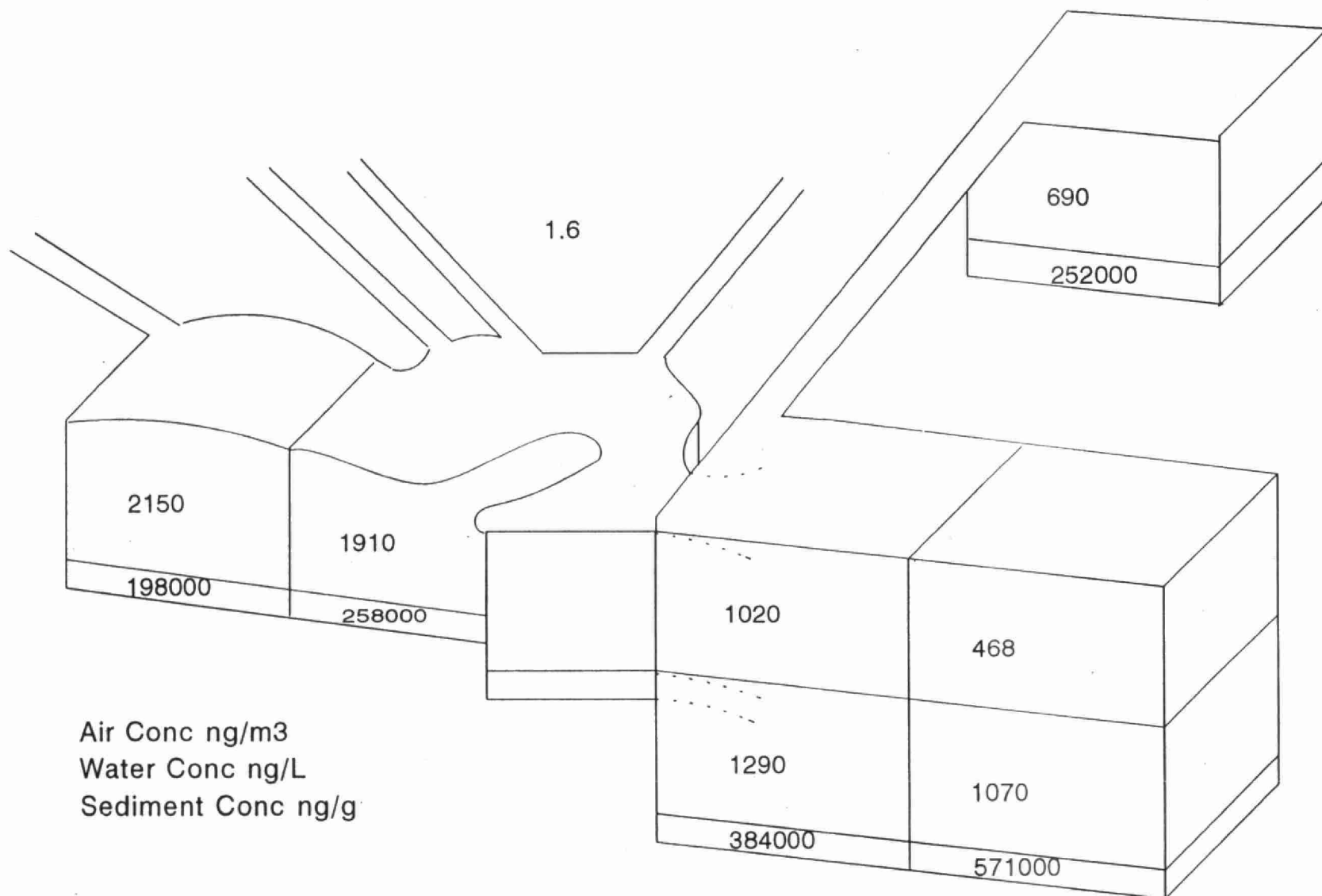1020

468

1290

1070

384000

571000

Figure 10: Updated conditions, lead concentrations
in water and sediment.
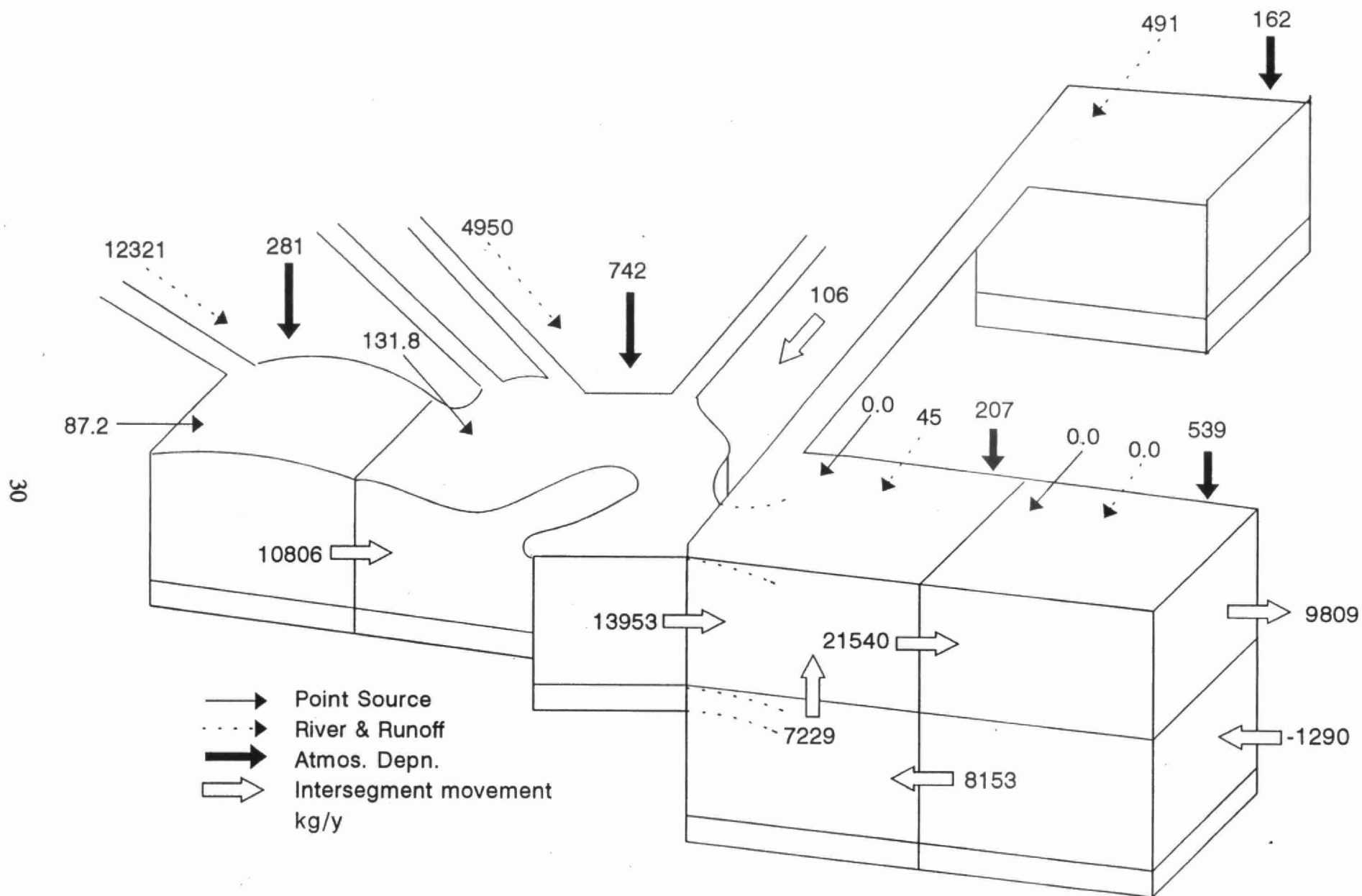
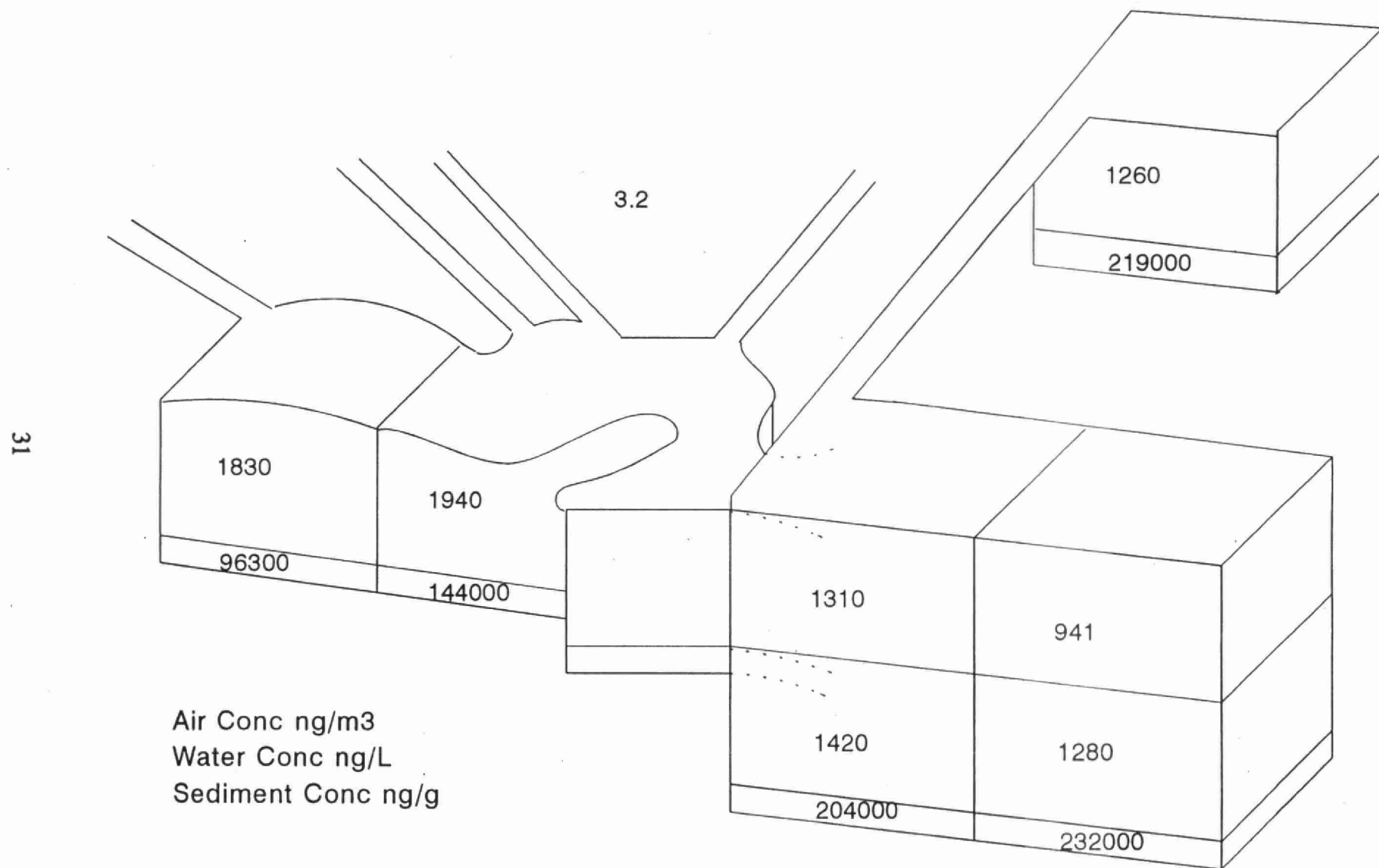Figure 11: Updated conditions, estimates of loadings and chemical movement for lead.

30

1260

219000

3.2

1830

1940

96300

144000

1310

941

1420

1280

204000

232000

Air Conc ng/m3
Water Conc ng/L
Sediment Conc ng/g

Figure 12: Updated conditions, zinc concentrations
in water and sediment.
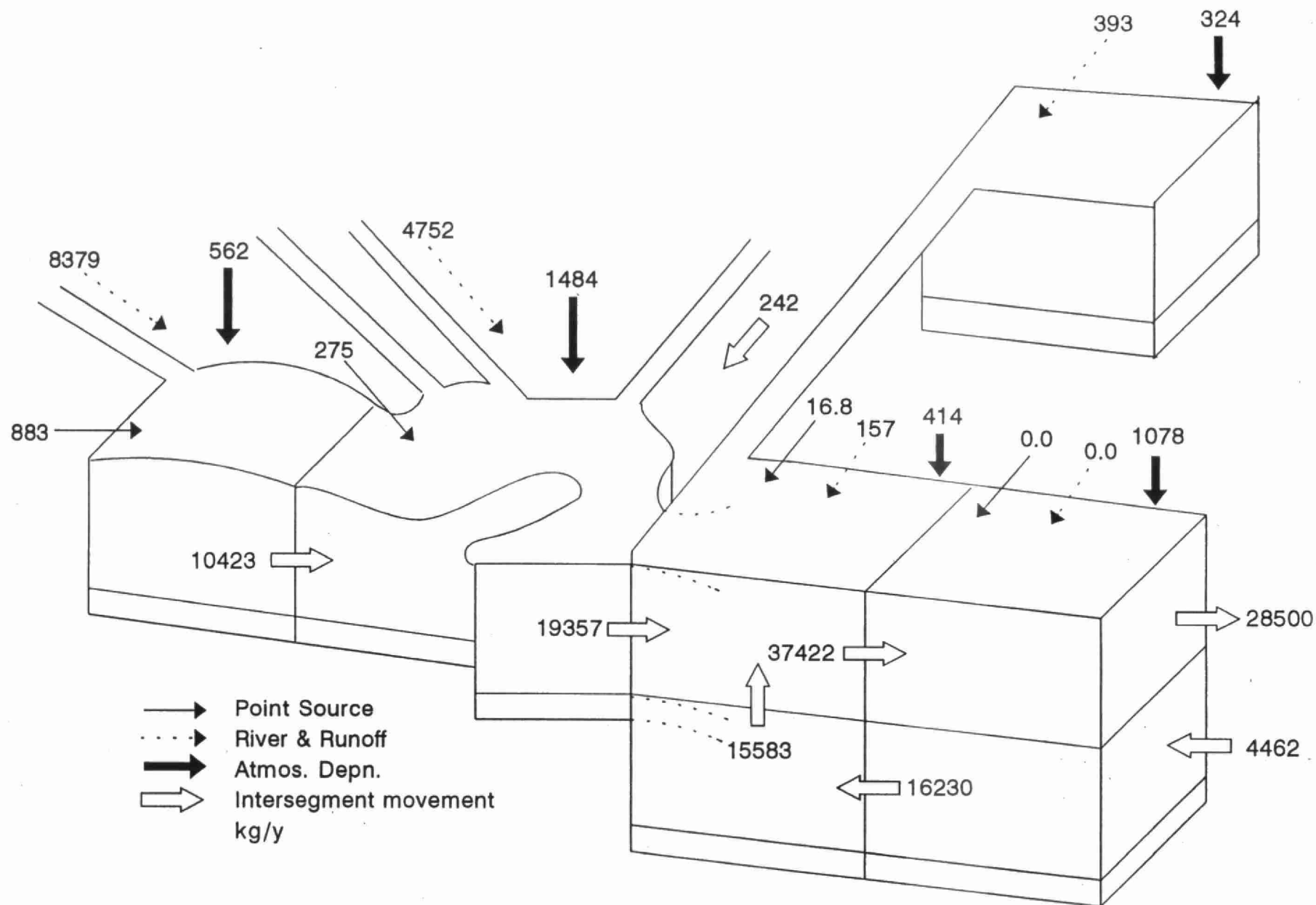
Figure 13: Updated conditions, estimates of loadings and chemical movement for zinc.

In order to decrease sediment zinc concentrations to below the LEL, external inputs to the Bay, including tributary and atmospheric, will have to be reduced. As seen in Figure 13, point sources represent a small fraction of the total input.

4.6   Chloroform

Chloroform concentrations in the various media are given in Figure 14, while inputs and intersegment movements are given in Figure 15. Point source data for the pulp and paper sector have been estimated from the MISA control regulation, and are actually higher than 1988 data used by Diamond et al. (1992); however, as they contribute only a small (25% or less) contribution of total loads to segments 1, 2 and 4, and nothing to other segments, the calculated concentrations in all media are similar to those calculated previously. Concentrations of chloroform in sediment and fish are very low on account of its high volatility and low log K_{ow}.

No water or sediment objectives exist for this chemical. These model results using BATEA limits suggest that the present level of control is adequate in the Bay of Quinte. However, tributary and atmospheric data are approximations as used by Diamond et al. (1992), and limit the accuracy of model predictions for this chemical.

4.7   Pentachlorophenol

Pentachlorophenol (PCP) concentrations in the various media are given in Figure 16, while inputs and intersegment movements are given in Figure 17. A considerable decline between 1988 and 1993 in point source loadings has resulted in an over 80% reduction in water concentrations in Upper Bay west and east segments. PCP concentrations in fish have also decreased by a factor of about 6 in these segments. Moving towards the lake, the extent of decrease is lower; however, absolute concentrations of PCP still decline as one moves away from the source at Trenton.

Tributary loadings in Upper Bay segments are now similar to point source loadings. These were based on 1988 data and thus may represent an overestimate; if so, modelled concentrations in the Upper Bay may still be overestimates.

Otherwise, contributions from Lake Ontario and the atmosphere are negligible. The PCP concentration declines rapidly as one moves downstream, due to its rapid transformation to lower chlorinated phenols and hydroquinones. Negligible
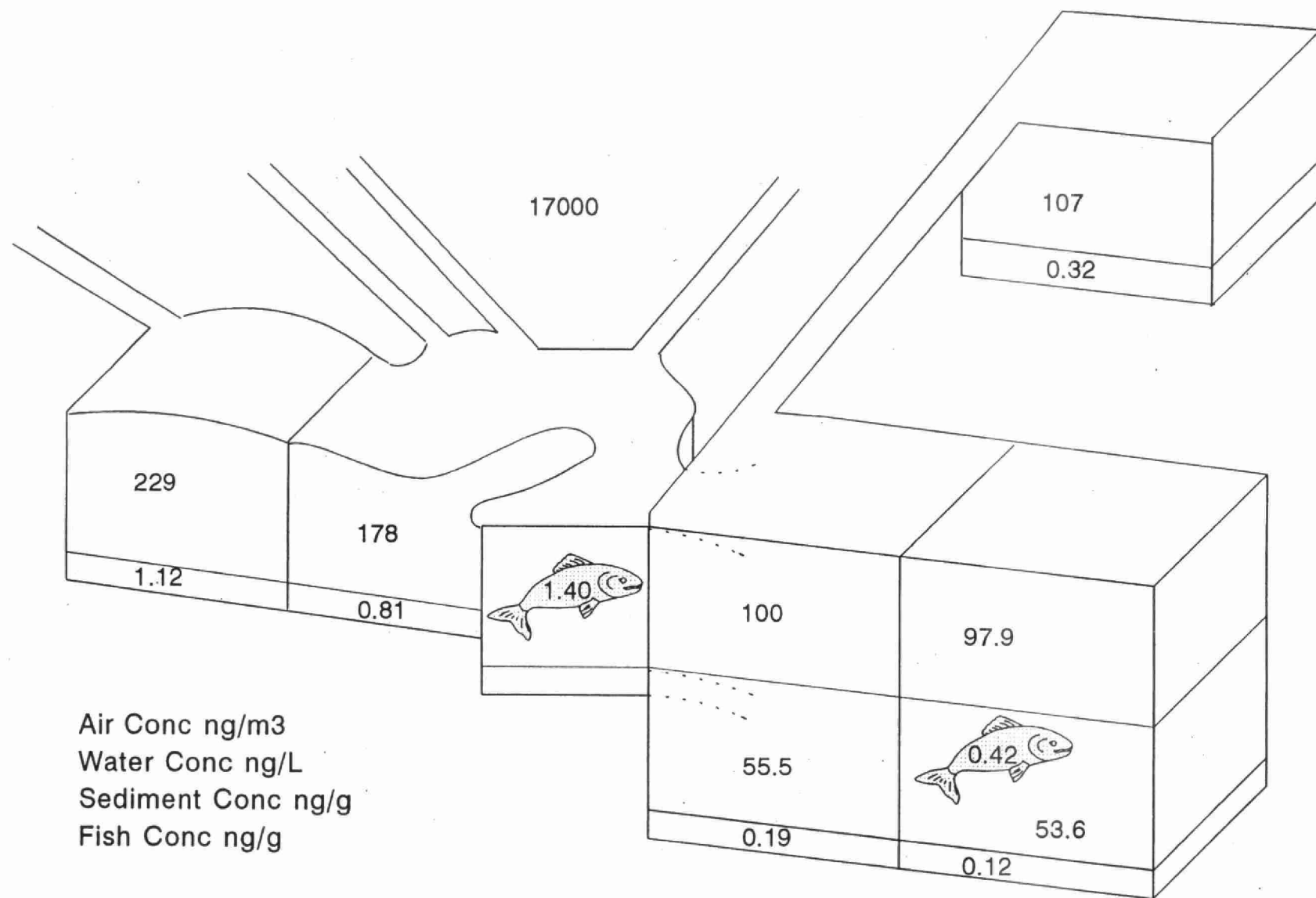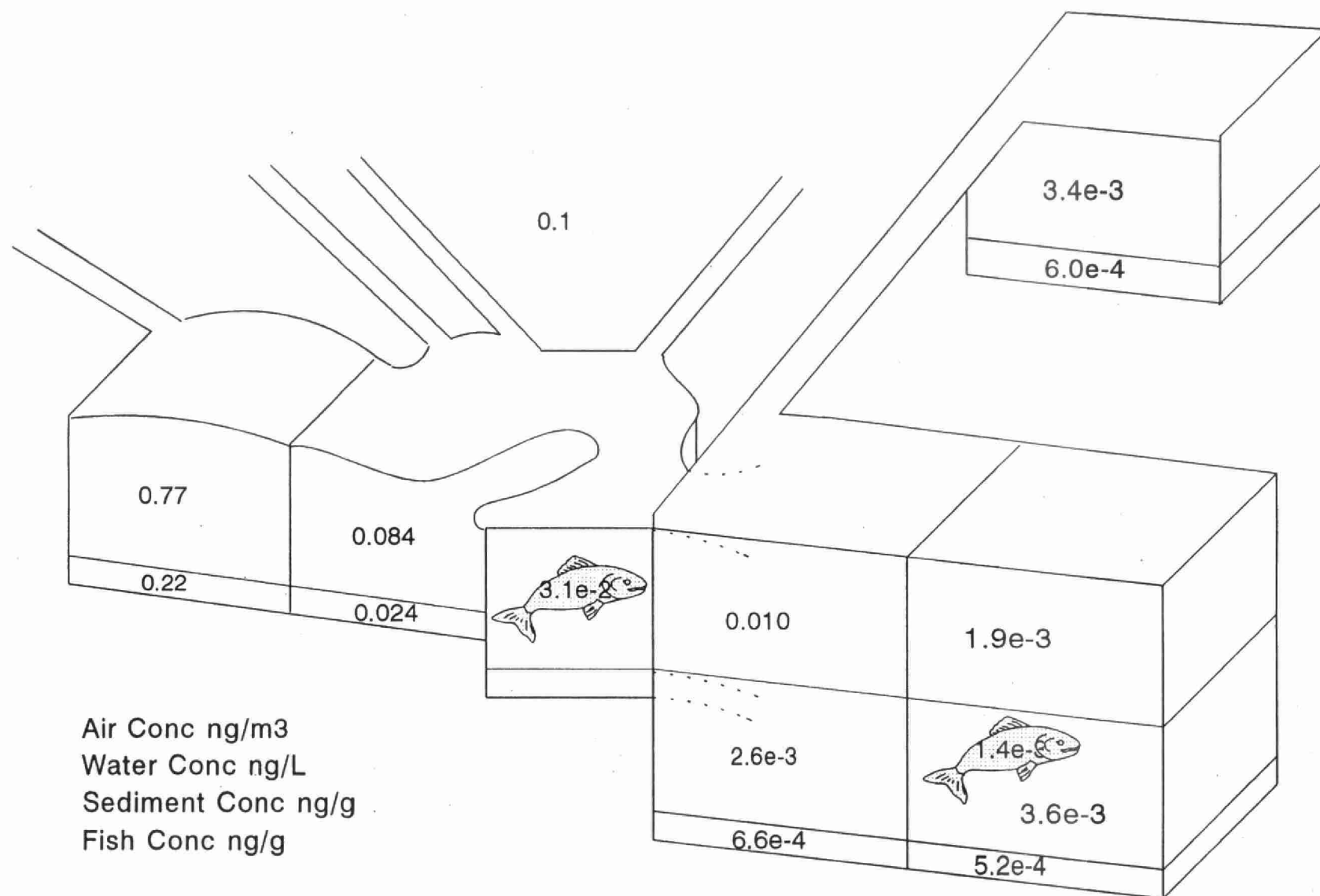
33

17000

107

0.32

229

178

1.12

0.81

1.40

100

97.9

Air Conc ng/m3
Water Conc ng/L
Sediment Conc ng/g
Fish Conc ng/g

55.5

0.42

0.19

53.6

0.12

34

Figure 14: Updated conditions, chloroform concentrations
in water, sediment and fish.

1.9   2.3

495.0

1232.1   4.0   10.5   21.5

142.0

306.2   6.2   23.8   2.9   0.0   0.0   7.6

35

1173

1301   2013

2025

642   644

646

Point Source
River & Runoff
Atmos. Depn.
Intersegment movement
kg/y
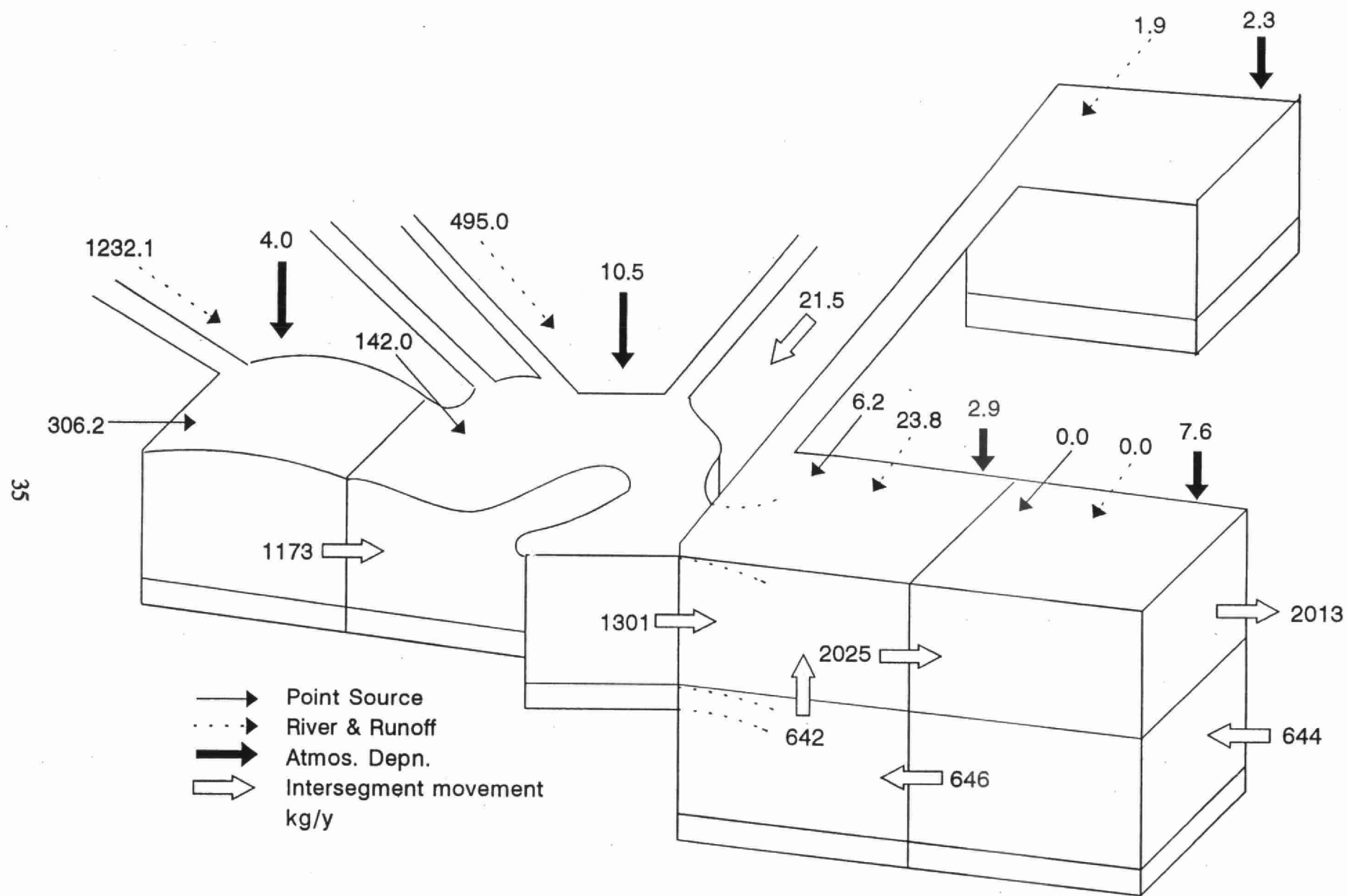
Figure 15: Updated conditions, estimates of loadings and
chemical movement for chloroform.

0.1

3.4e-3

6.0e-4

0.77

0.084

0.22

0.024

3.1e-3

0.010

1.9e-3

2.6e-3

1.4e-3

3.6e-3

6.6e-4

5.2e-4

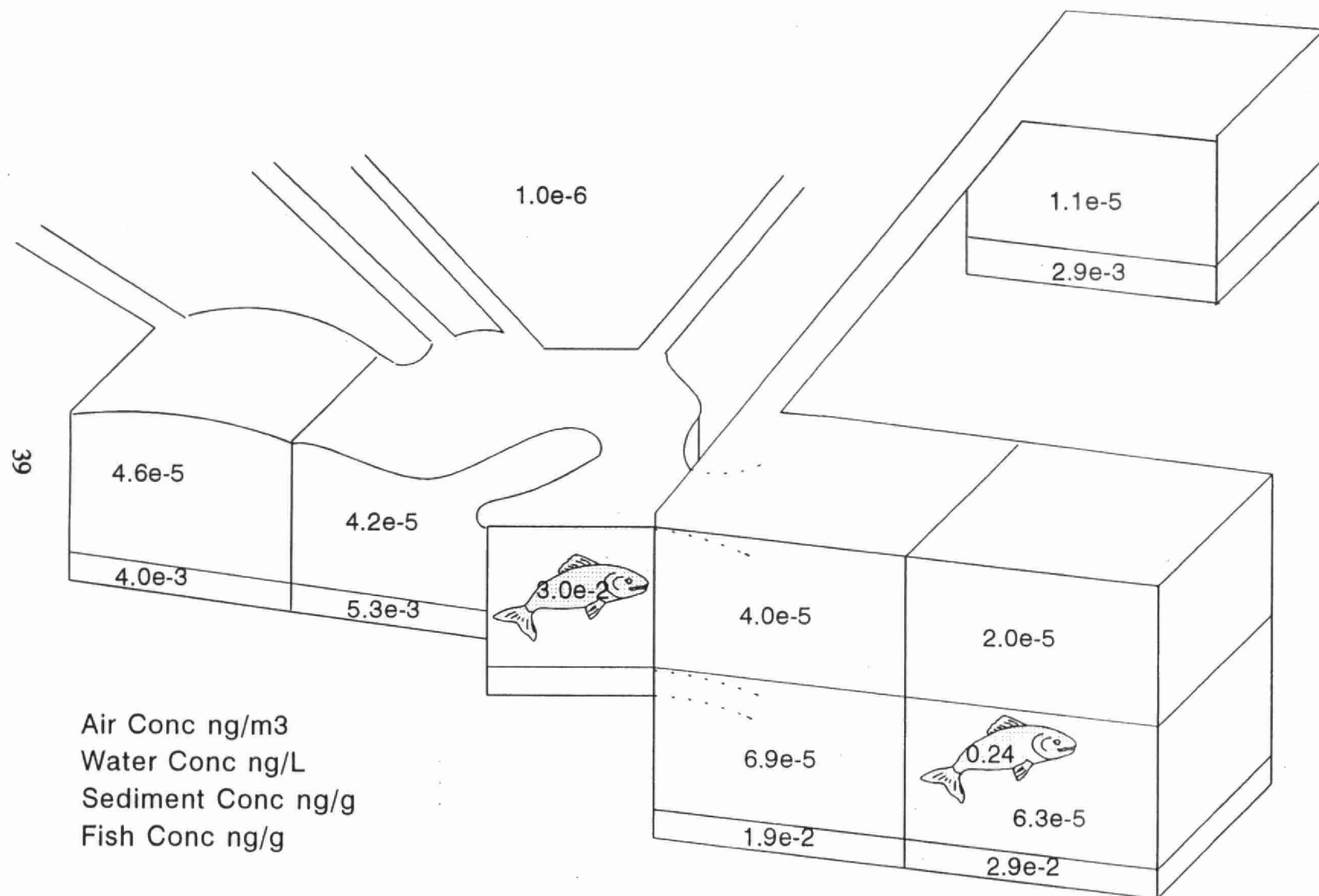Air Conc ng/m3
Water Conc ng/L
Sediment Conc ng/g
Fish Conc ng/g

Figure 16: Updated conditions, PCP concentrations
in water, sediment and fish.

36
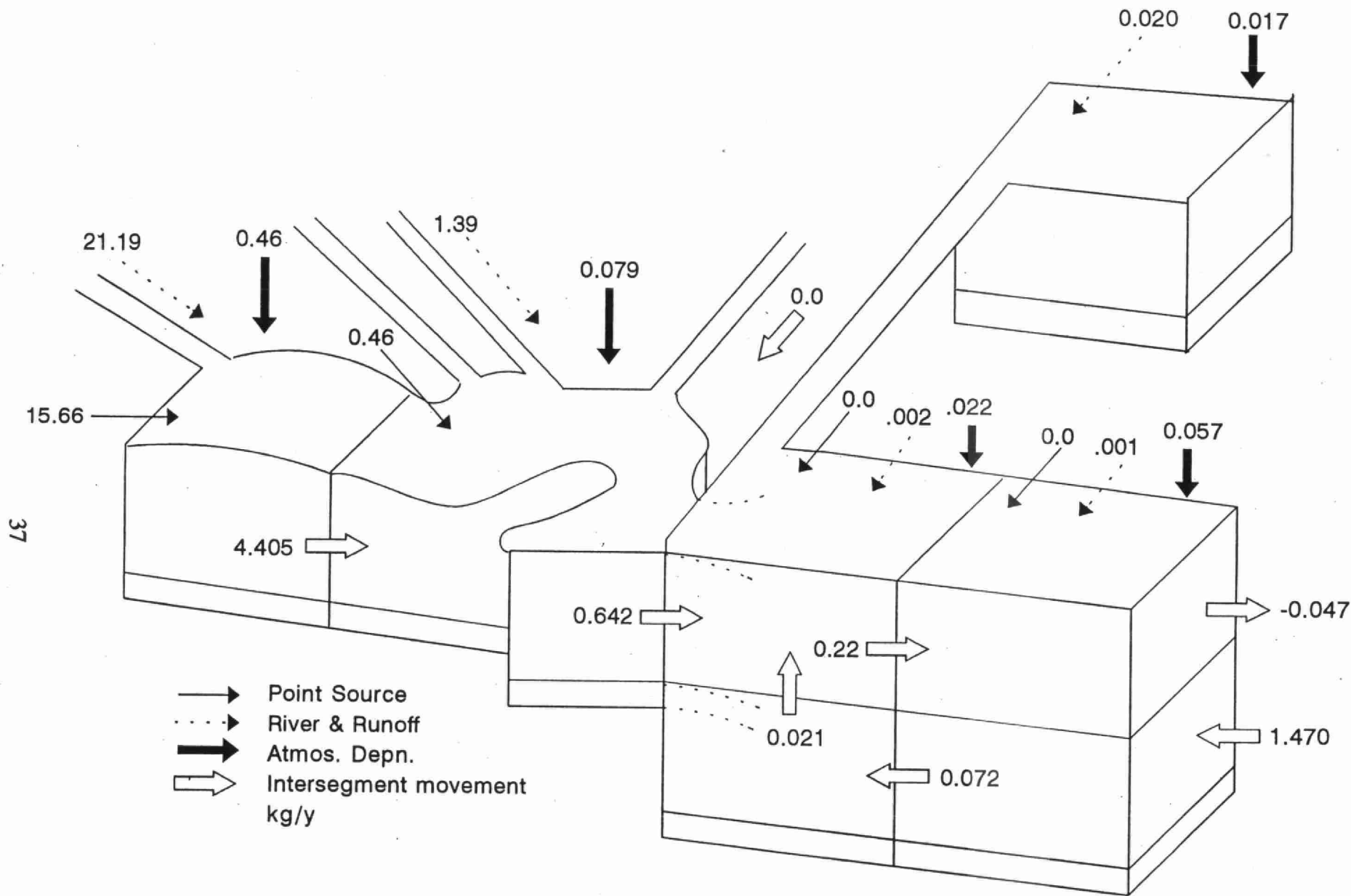
Figure 17: Updated conditions, estimates of loadings and chemical movement for pentachlorophenol.

volatilization and sedimentation occur, because of PCP's relatively low Henry's Lawconstant and log K_{ow}.

This result shows the rapid decline achieved from recent decreases in industrial discharges. In order to verify the predicted concentrations, additional measurements using low-level techniques such as the Goulden extractor would be beneficial.

4.8 TCDD and TCDF

Concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF and their inputs and movements are given in Figures 18-21. As stated previously, the MISA pulp and paper regulation states that these compounds be below their RMDL; point source concentrations have been estimated as 0.1 * RMDL. At these values, TCDD levels are mainly controlled by Trent River inputs and exchange with Lake Ontario; atmospheric input of TCDF is slightly higher than other inputs, however all inputs are of a similar order of magnitude. All modelled results are similar to those of Diamond et al. (1992).

As with Diamond et al. (1992) these results are only a rough first approximation at modelling these compounds, due to their extremely low levels. Atmospheric input was estimated (M. Diamond, pers. comm.) in order to give reasonable agreement between observed and predicted fish TCDD and TCDF levels. The amount of deposition may be as high as 0.2 g/yr, as estimated from air concentrations in the northern U.S. (Eitzer and Hites, 1989). The lack of more recent fish data as mentioned above precludes more accurate modelling of these compounds. It is also not possible to indicate whether or not further remediation of input sources is needed.

1.0e-6

1.1e-5

2.9e-3

4.6e-5

4.2e-5

4.0e-3

5.3e-3

3.0e-2

4.0e-5

2.0e-5

6.9e-5

0.24

6.3e-5

1.9e-2

2.9e-2

Air Conc ng/m3
Water Conc ng/L
Sediment Conc ng/g
Fish Conc ng/g

Figure 18: Updated conditions, 2,3,7,8-TCDD concentrations
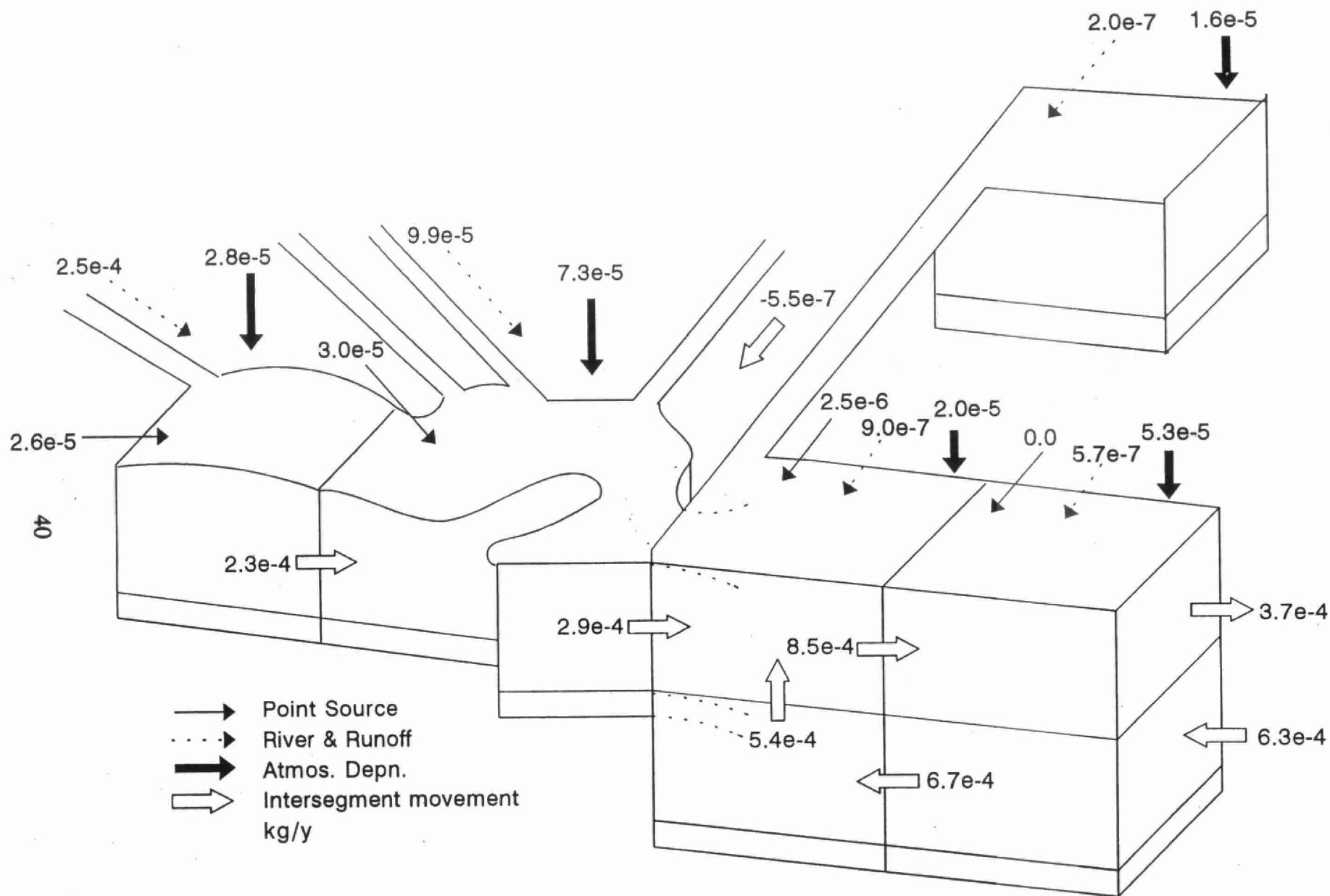in water, sediment and fish.

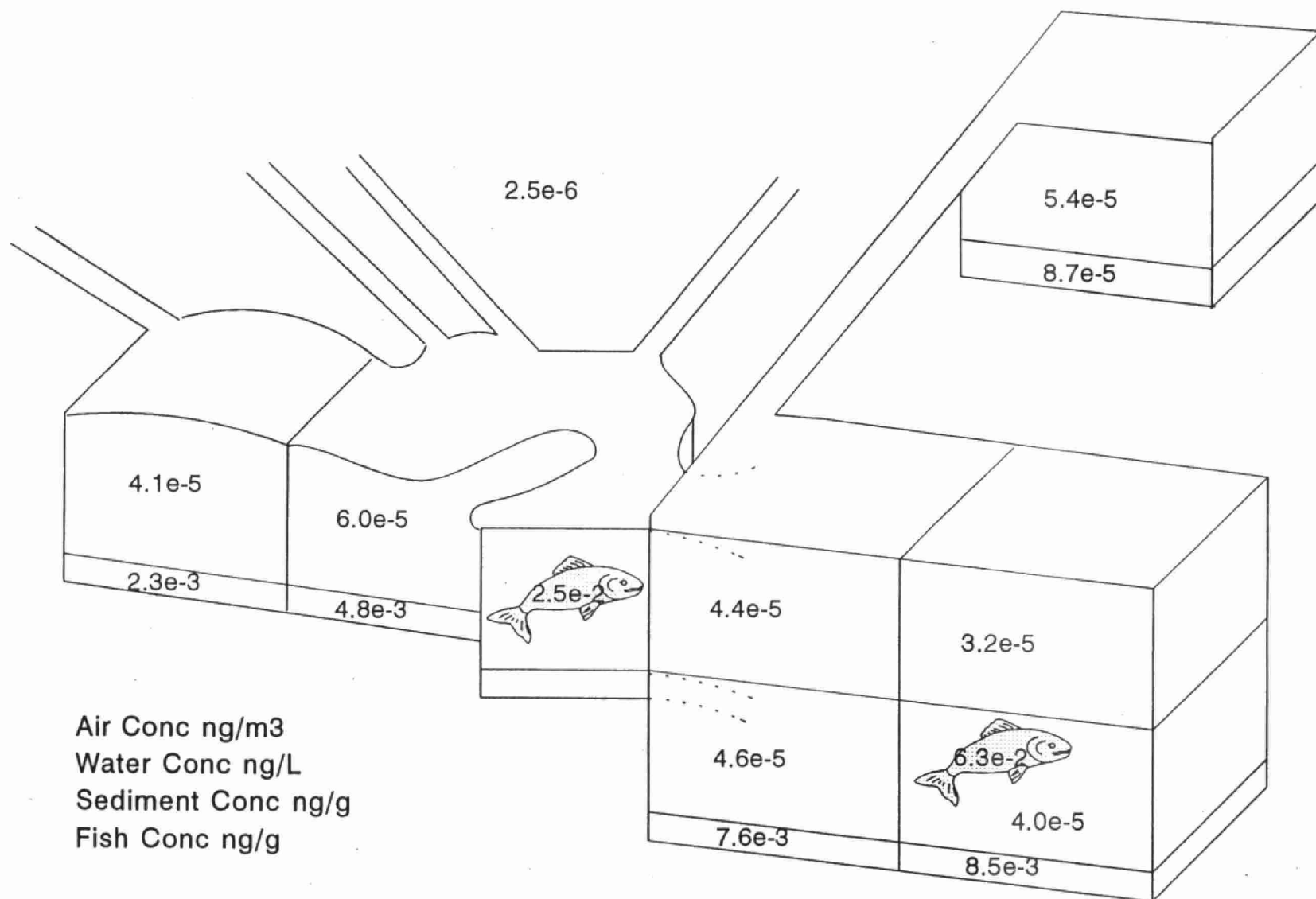Figure 19: Updated conditions, estimates of loadings and chemical movement for 2,3,7,8-TCDD.

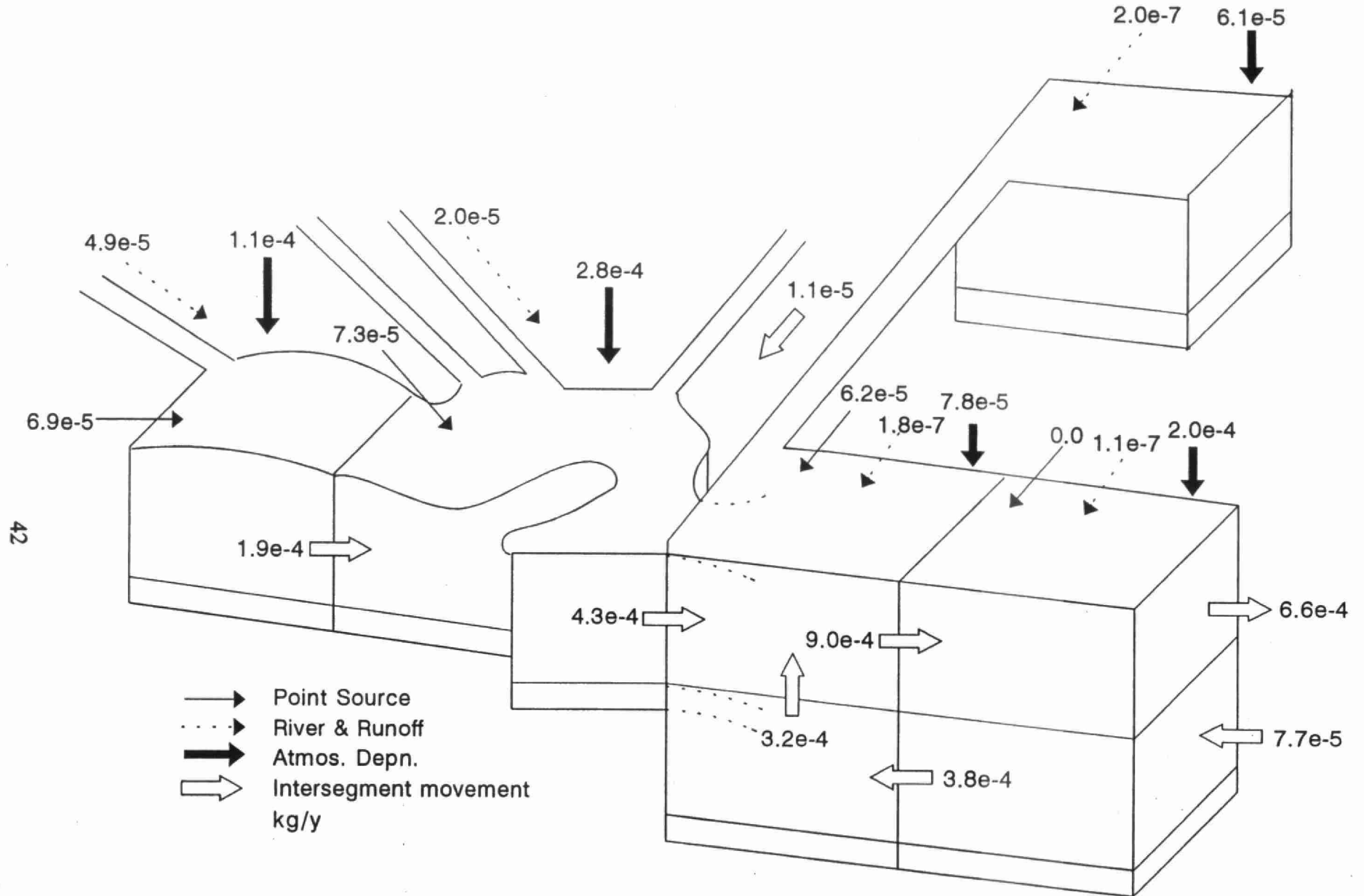Figure 20: Updated conditions, 2,3,7,8-TCDF concentrations in water, sediment and fish.

2.5e-6

5.4e-5

8.7e-5

4.1e-5

6.0e-5

2.3e-3

4.8e-3

2.5e-2

4.4e-5

3.2e-5

4.6e-5

6.3e-2

4.0e-5

7.6e-3

8.5e-3

Air Conc ng/m3
Water Conc ng/L
Sediment Conc ng/g
Fish Conc ng/g

41

Figure 21: Updated conditions, estimates of loadings and chemical movement for 2,3,7,8-TCDF.

5.0 DISCUSSION

The credibility of model predictions is only as good as that of the data input to the model. It has been observed that for many parameters, "non-detect" concentrations in tributary water and source inputs has limited the accuracy of model calculations. Even when there are good estimates of most input data (as with most metals), uncertainties in chemical-specific constants can limit the accuracy of the output. This has been shown by the unreasonably high sediment concentrations of many parameters in Hay Bay, which is relatively isolated and receives very little land-based input. The atmosphere was found to be the major input of all modelled metals to Hay Bay, a fact that causes the large differences observed here between these data and those of Diamond et al. (1992), who used assumed input values which were much smaller than those measured in the MOEE ambient air monitoring studies (Table 5; MOEE, 1994).

Diamond and Mackay (1991) explored the sensitivity of model predictions for arsenic, PCP and PCBs to model physical parameters such as sediment depth, river flow, water exchange, diffusion, degradation rate (organics), etc, by doing runs in which they doubled or halved the values of these parameters. They found model results to be quite sensitive to active sediment depth, porosity, deposition, resuspension, and K_p (water-suspended particle partition coefficient) (for inorganics) and degradation rate (for organics). However, it should be mentioned that their sensitivity calculations were only bases on total mass of chemical in water and sediment. One consequence of this is the sensitivity to sediment depth. Doubling the sediment depth doubles the amount of chemical in the active sediment layer without changing its concentration. (and vice versa). In this study, *concentrations* of chemicals were examined. This shows up the true insensitivity of the model to active sediment depth thickness. They did not explore the sensitivity of model predictions to uncertainties in input data, particularly where inputs had to be "back-calculated" from fish concentrations and could have been affected by food chain parameters as well as the relative value of different inputs (atmospheric, point source, tributary, etc.)

As testing the sensitivity of the modelled results to calibrated parameters represents a means by which the need for accurate measurement of such parameters can be assessed, a sensitivity analysis was run using the updated input. Values of the following parameters were doubled and halved individually, and the model response tested by comparing the resultant concentrations to those of the "base case" as

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described above: Sediment depth, concentration of suspended particulates, sediment porosity, tributary river flow (multiplied by 2/3 and 3/2), intersegment water exchange, particulate deposition, particulate resuspension from the bed, and sediment burial to the inactive layer. Also, for inorganics only, Kp for suspended particulate-water exchange and Kp for bottom sediment-water exchange. For organics only, particulate organic carbon content, sediment organic carbon content, log Kow (varied by ± 0.5), degradation rate in water and sediments respectively, water solubility, and vapor pressure. Abbreviations used for these scenarios are given below in Table 9.

The results are given as bar graphs of percent base case for each segment in water (top panel) and sediment (bottom panel) in the following figures. Parameters with less than 10% deviation from base case have been omitted from the plots in individual parameters, to improve clarity.

TABLE 9

ABBREVIATIONS USED IN SENSITIVITY ANALYSIS FIGURES

Parameter	Abbreviation
Sediment depth	sed. dep.
Concentration of suspended particulates	CSP or conc. susp. part.
Sediment porosity	porosity
Tributary river flow	rflow
Intersegment water exchange	wexch
Particulate deposition	depn or deposition
Particulate resuspension from the bed	resus or resuspension
Sediment burial to the inactive layer	bur or burial
Kp for suspended particulate-water exchange	Kppw
Kp for bottom sediment-water exchange	Kpsw
Degradation rate	degrad
Log octanol-water partition coefficient	Log Kow
Water solubility	soly
Vapor pressure	vap. press.

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5.1   Sensitivity analysis for inorganic parameters (As, Cd, Cu, Pb and Zn)

The sensitivity analysis for arsenic is given in Figure 22.   In water, nearly all parameters are quite insensitive. River flow and water exchange in segment 1 are the most sensitive, as they influence the back-exchange of high-As water in segment 2 (Upper Bay East, where the principal input of As is) to segment 1. Sediment-related parameters have little effect on water arsenic concentration as arsenic is predominantly found in the dissolved form; however, because of this fact, doubling the depositional rate approximately doubles sediment As concentrations, while halving the resuspension rate has almost as great an effect. A similar effect is observed if the particle-water Kp is doubled. Sediment concentrations are halved by the opposite change in these parameters. Parameters such as the sediment resuspension and deposition rate can vary widely both seasonally and spatially; if a high-quality time-dependent model of arsenic is needed, additional measurements of these parameters would be very important.

The sensitivity analysis for cadmium is given in Figure 23. Unlike arsenic, cadmium has a greater affinity for sediments (but less than, for example, lead and zinc). Thus sediment-related parameters have an effect on cadmium levels in water, especially in shallow Hay Bay (e.g. concentration of suspended particulates, deposition, burial, and resuspension. These parameters (particularly deposition) have a profound effect on sediment cadmium levels, resulting in an approximate doubling for doubling the deposition rate in the Lower Bay but cutting the sediment cadmium to less than 40 percent of base case for halving the deposition rate in the same segment.

Copper levels in water are quite insensitive to all parameters (Figure 24, top panel). As with arsenic, sediment copper concentrations are very sensitive to doubling of deposition rates and Kp (particulate-water), and halving of resuspension rates, but only slightly sensitive to the value of Kp (sediment-water).

The sensitivity analysis for lead is given in Figure 25. Lead (and zinc) have the greatest affinity for sediments of all metals modelled in this study, and consequently have a high sensitivity in both the water column and sediment to values of suspended particulates, deposition, resuspension, and burial. This appears to be particularly true in the Middle and Lower Bays, and in water for Hay Bay. The effect of river flow and water exchange rates appears to increase gradually as one moves downstream (towards Lake Ontario); this would be a loading effect as the concentration in both

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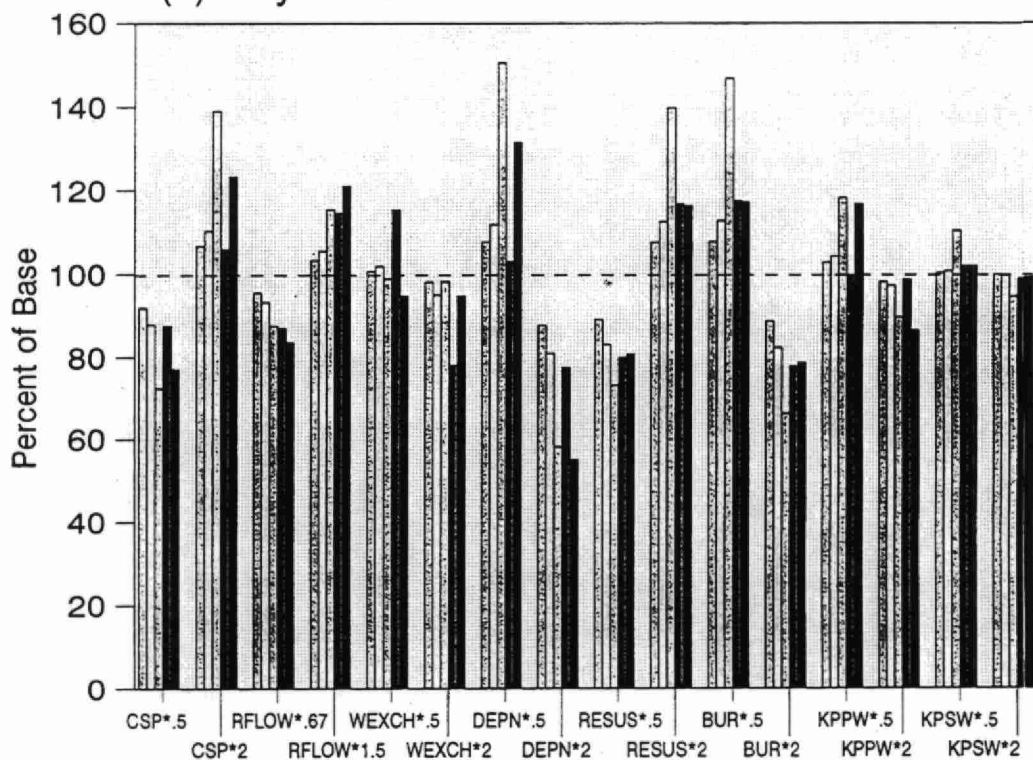# Figure 22: Sensitivity analysis for arsenic

(a) Bay of Quinte water
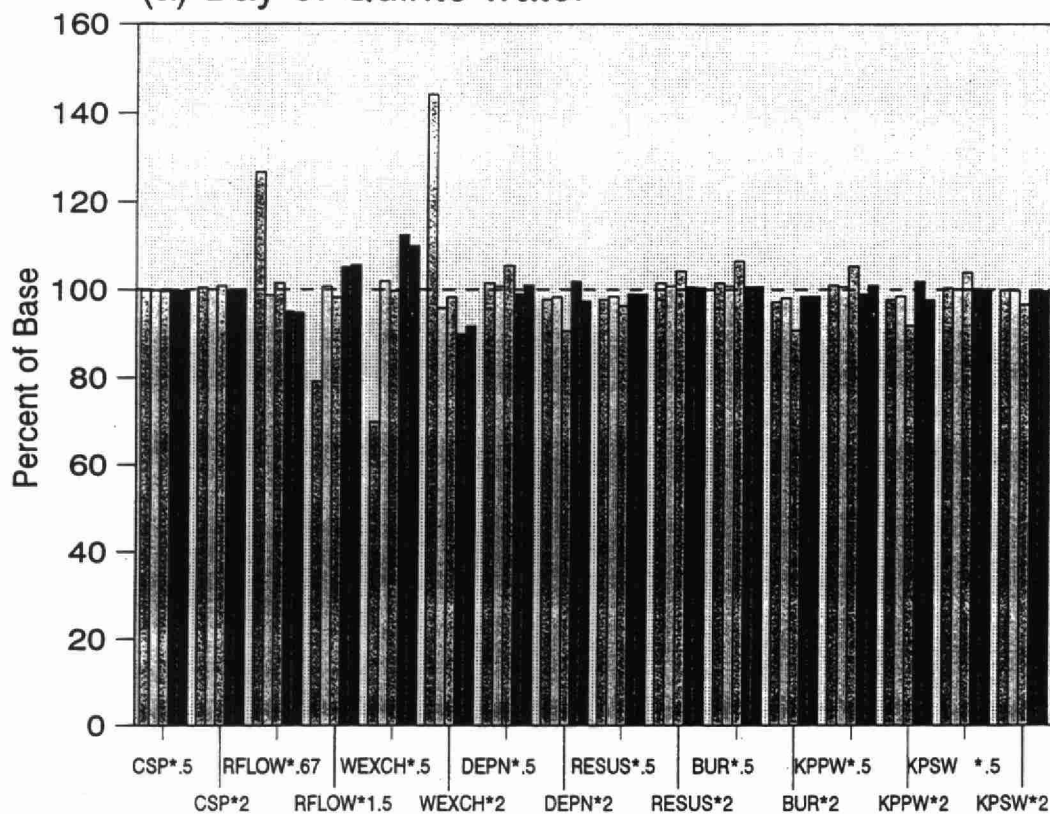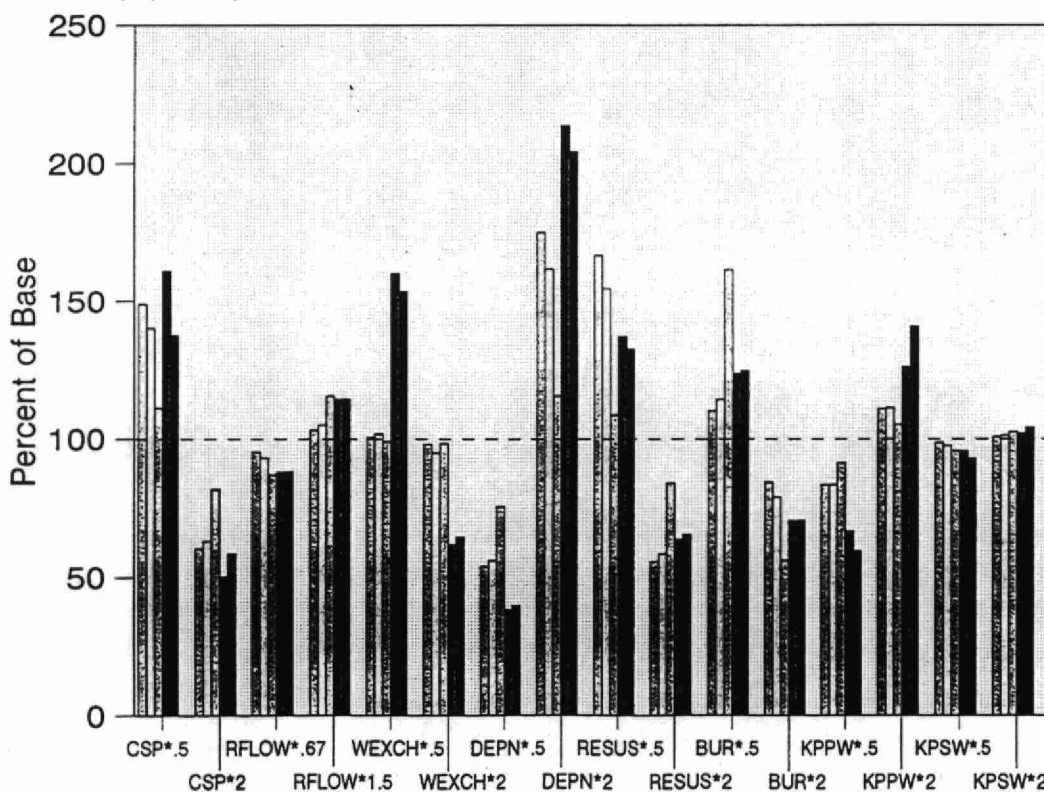

(b) Bay of Quinte Sediments

Upper Bay W   Upper Bay E   Hay Bay   Middle Bay   Lower Bay

46
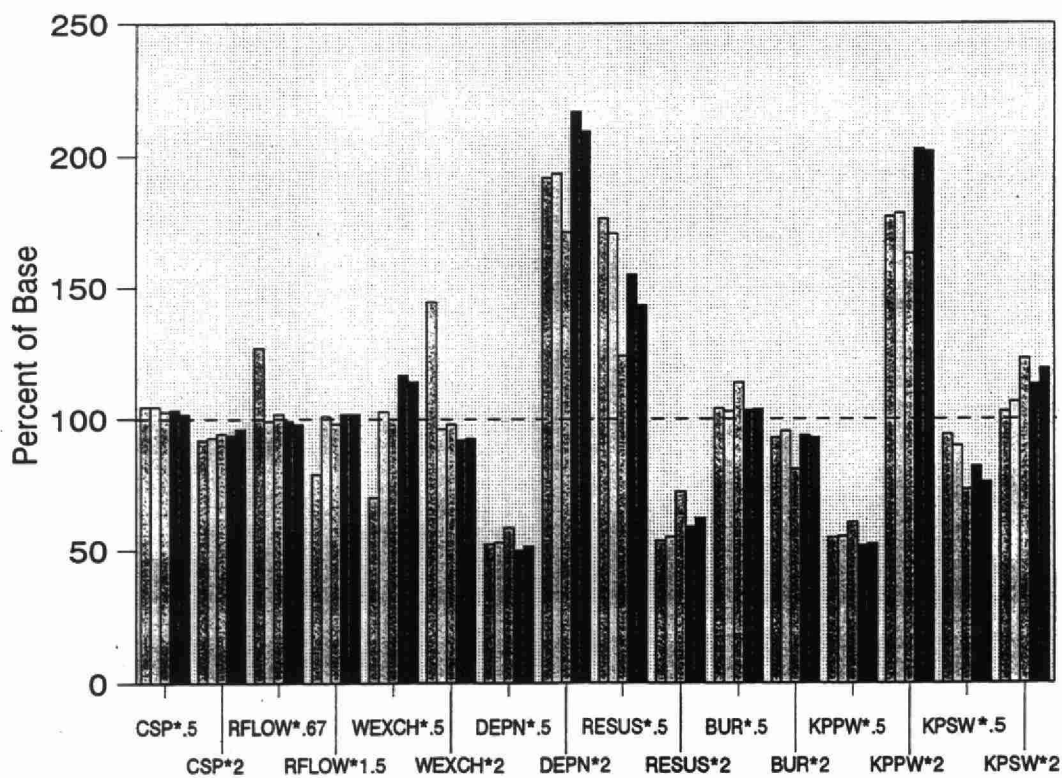
Figure 23: Sensitivity analysis for cadmium
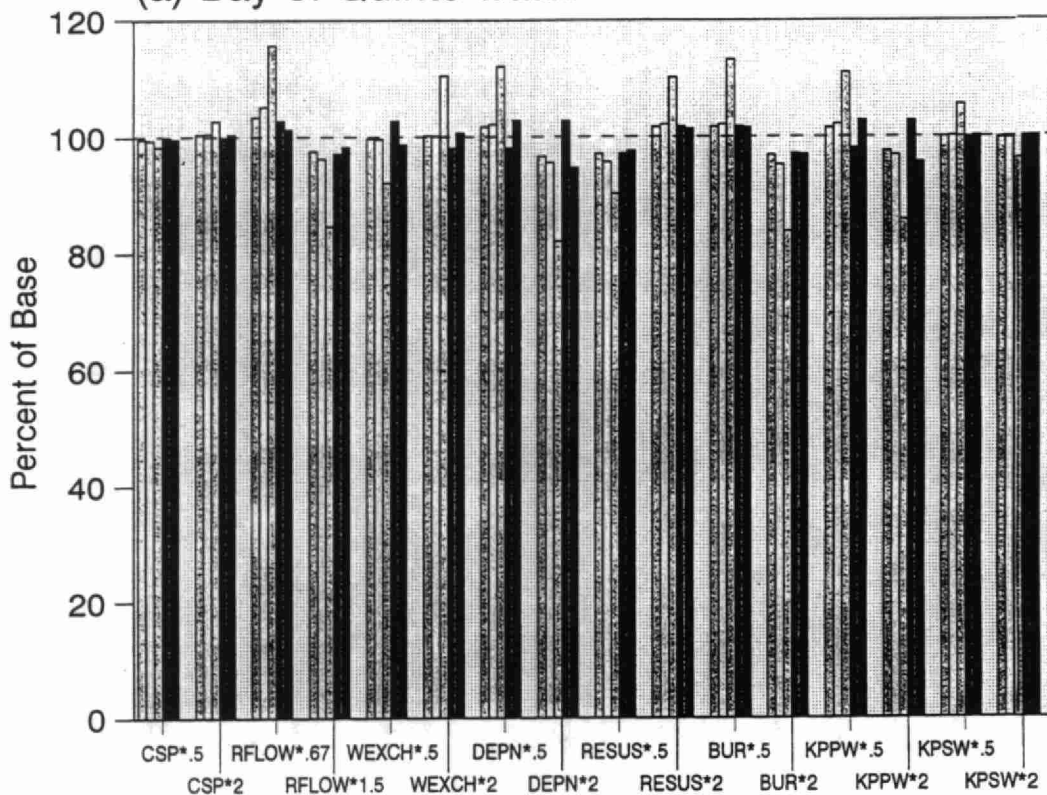
(a) Bay of Quinte water
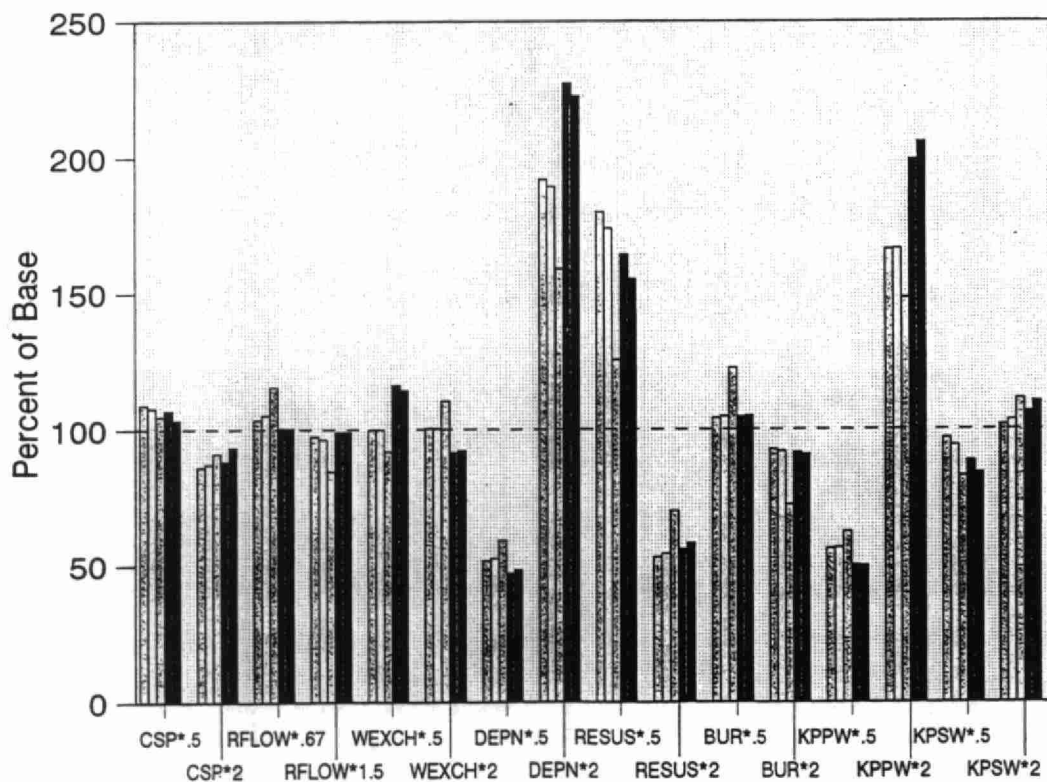

(b) Bay of Quinte sediments

Upper Bay W   Upper Bay E   Hay Bay   Middle Bay   Lower Bay

Figure 24: Sensitivity analysis for copper

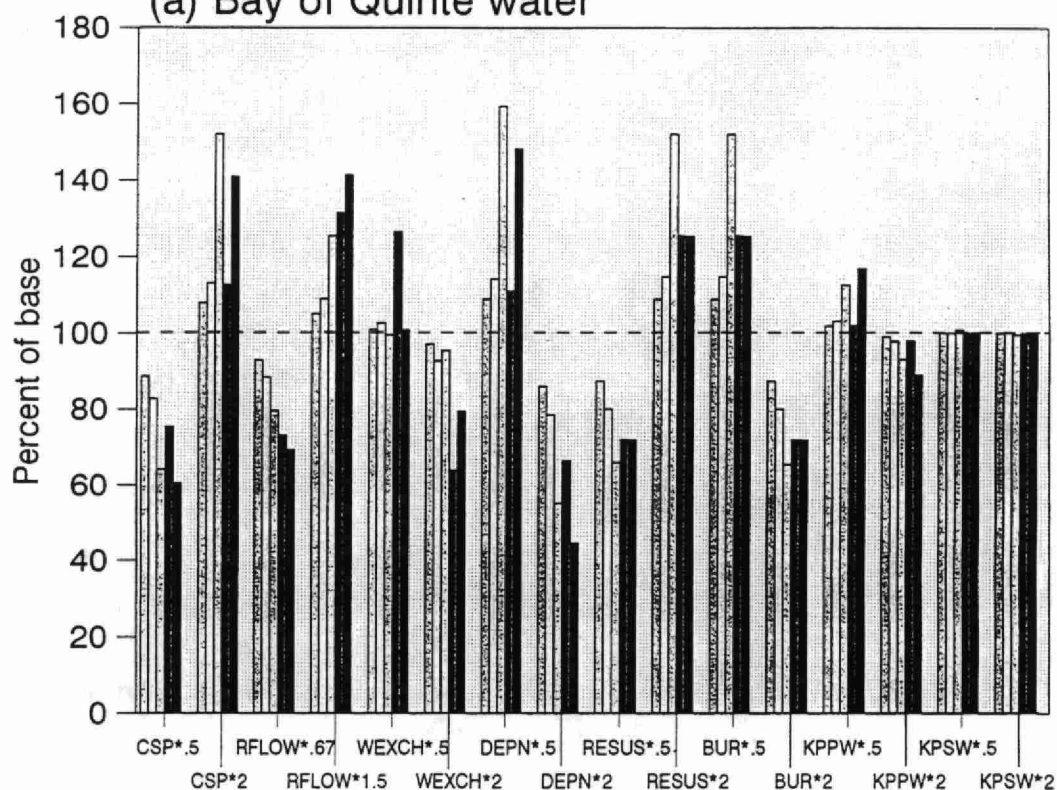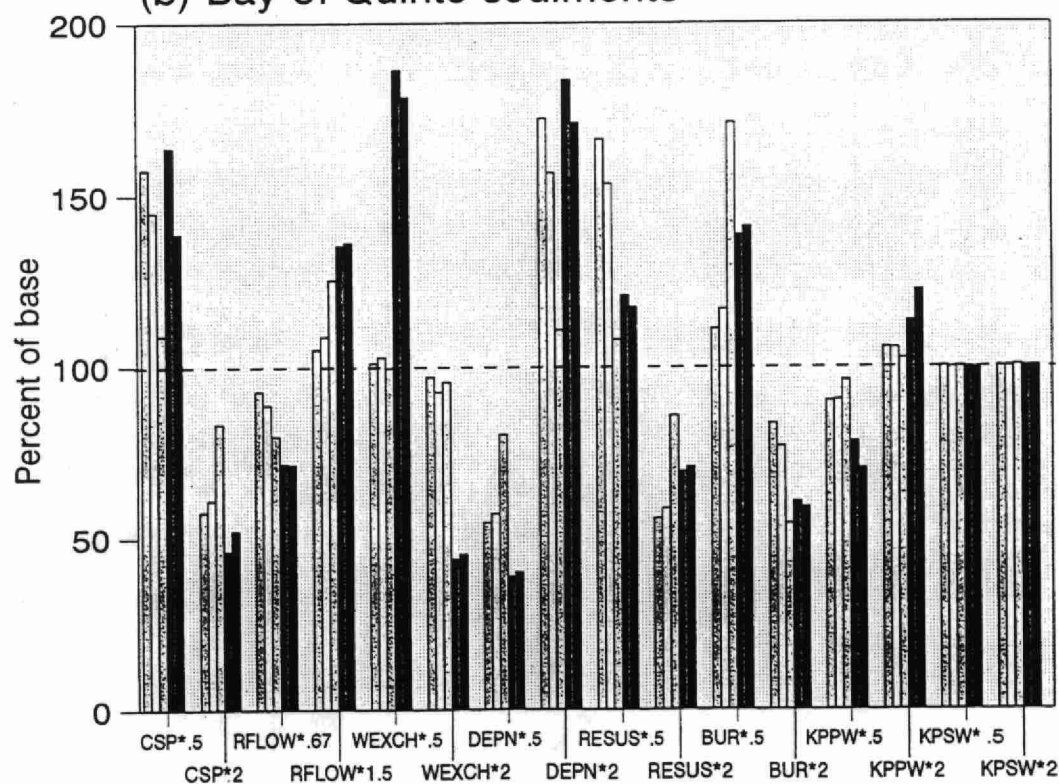## (a) Bay of Quinte water

(b) Bay of Quinte sediments

Upper Bay W Upper Bay E Hay Bay Middle Bay Lower Bay

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Figure 25: sensitivity analysis for lead

(a) Bay of Quinte water

(b) Bay of Quinte sediments

Upper Bay W Upper Bay E Hay Bay Middle Bay Lower Bay

media increase progressively with the 1.5 increase in river flow. Decreasing water intersegment exchange to 50 percent almost doubles sediment lead concentration in Middle and Lower Bays, but has very little effect on this parameter in other segments. The reason for this disparity is unknown.

The behavior of zinc (Figure 26) is similar to that of lead, but is somewhat less sensitive for most parameters, except K_p (particle-water) and deposition, as noted below. (It should be noted that both lead and zinc are very insensitive [less than 1% for Pb and 5% for Zn] to the value of K_p [sediment-water]). Doubling of sediment depositional rates more than doubles the sediment concentration in Hay Bay and Lower Bay, but has little effect on Middle Bay.

It appears that accurate measurement of parameters related to sediment-water exchange of inorganic parameters has the greatest bearing on accurate modelling of inorganics. It should be noted that this does not include values for inputs from point sources or tributaries, or atmospheric inputs; the latter in preliminary runs was seen to be quite a sensitive parameter, from the varied results of recent atmospheric surveys, together with the disparities between recently measured and assumed (Diamond et al. 1992) air concentrations. The model also does not address the influence of organic substances which can complex the metals and thus retain them in solution, to be measured by the routine laboratory methods which measure total metals. Complexation of the metals also reduces their toxicity to biota and needs to be addressed. Work on the application of the MINTEQA2 speciation model (Allison et al., 1991) is underway, and is needed to further address this complication.

5.2   Sensitivity analysis for organic parameters (Chloroform, PCP, TCDD, and TCDF)

Modelled results for these parameters are, as stated previously, already much less accurate (to only speculative) because of a large number of non-detects among input parameters. However, the sensitivity analysis is still useful in discerning the approximate accuracy of the predictions of the effect of the promulgated MISA-BATEA pulp and paper regulations for these parameters. Sensitivity plots have been prepared in a similar manner to those for the inorganics, except that variables with less than a ± 20 percent effect on the base case have been omitted.

50

Figure 26: Sensitivity analysis for zinc

(a) Bay of Quinte water
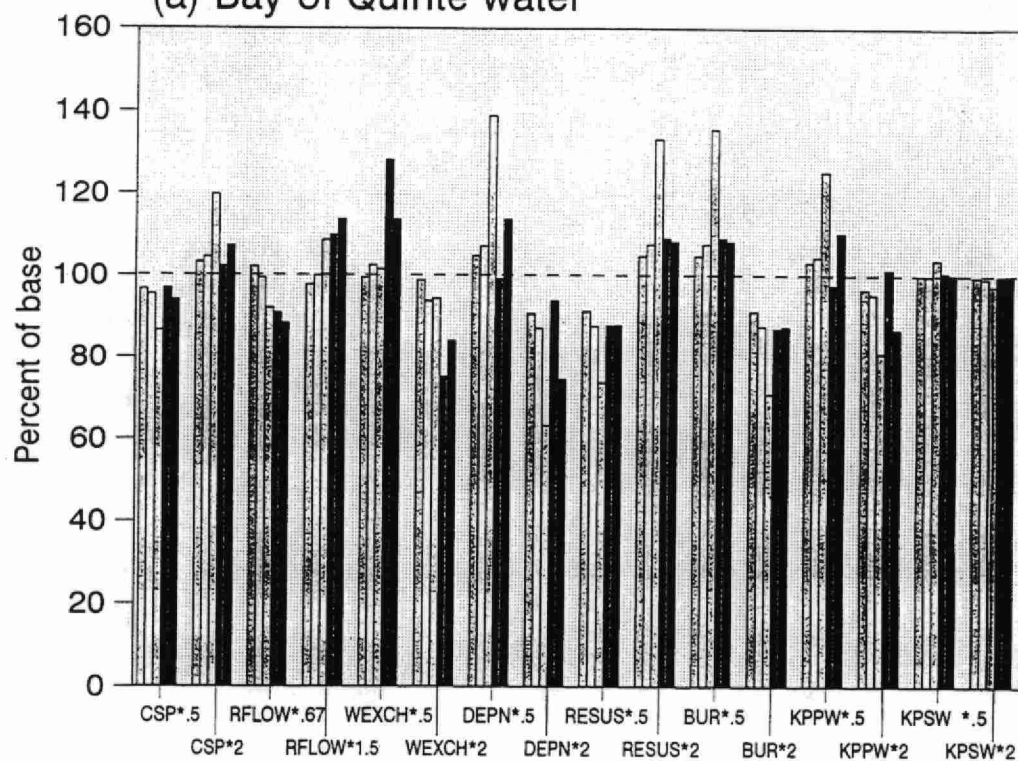
(b) Bay of Quinte sediments
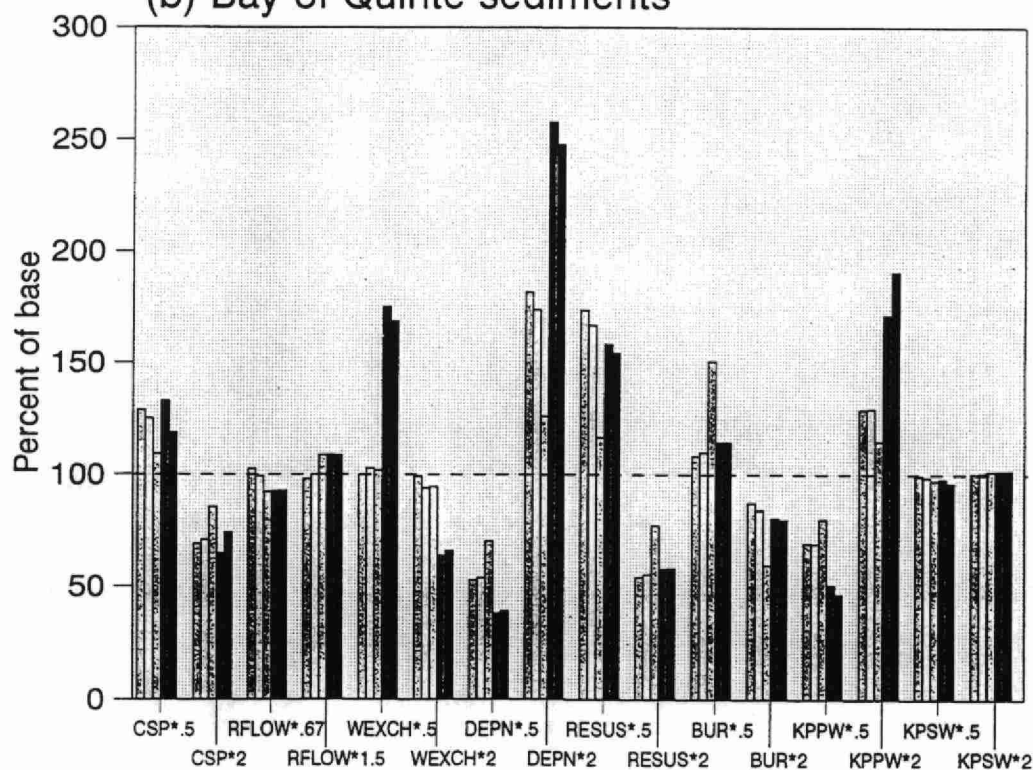
Upper Bay W　Upper Bay E　Hay Bay　Middle Bay　Lower Bay

Figure 27 gives the sensitivity analysis for chloroform in water and sediments. As this is a volatile chemical with low affinity for sediments, the only parameters with significant sensitivity in water are solubility (increased solubility increases chloroform levels) and vapor pressure (increased vapor pressure decreases chloroform levels). Increased organic content of sediments and increased K_{ow} both increase chloroform concentrations in sediment, without appreciably affecting water values (because the greatest percentage of chloroform is in the water; its K_{ow} is very low compared to the other organic chemicals).

Figure 28 gives the sensitivity analysis for PCP in water and sediments. This chemical is degraded rapidly to lower chlorinated phenols in water, and only about 1% is buried in the sediments. Thus the water PCP level is highly sensitive to the degradation rate; it is also sensitive to river flow and water exchange rate. In sediments, like chloroform, it is highly sensitive to the value of K_{ow}; it is also sensitive to degradation rate, and to a lesser extent to other sediment parameters. Again the latter are unimportant due to the small fraction of PCP occupying the sediments.

Figures 29 and 30 give the sensitivity analyses for TCDD and TCDF in water and sediments (separated and restricted to three segments for increased clarity). As these chemicals occur in these media at levels well below detection, this exercise is rather academic. Increased deposition or increased K_{ow} tend to decrease water levels and increase sediment levels as with the other organics; decreases in some sediment-related variables such as active depth, concentration of suspended particulates, porosity and resuspension as well as increased deposition tend to increase sediment TCDD and TCDF but have variable effects on water concentrations. It is better to compare levels of these chemicals in fish as this is where they are measurable and subject to control.

Figures 31-33 give the sensitivity analyses for organic chemicals in fish. It should be noted that levels of organics in fish will also be sensitive to food chain model parameters. These are beyond the scope of this study. Chloroform and PCP are, as might be expected, most sensitive to the value of log K_{ow}, with their concentrations increasing and decreasing by factors of about 3 for increases and decreases of 0.5 log units, respectively. Levels of chloroform are also moderately sensitive to increased solubility and decreased vapor pressure, resulting in an increase in concentration of a factor of almost 2 in shallow Hay Bay and less in other segments. Pentachloro-phenol exhibits a similar but smaller pattern with regard to these two parameters. It
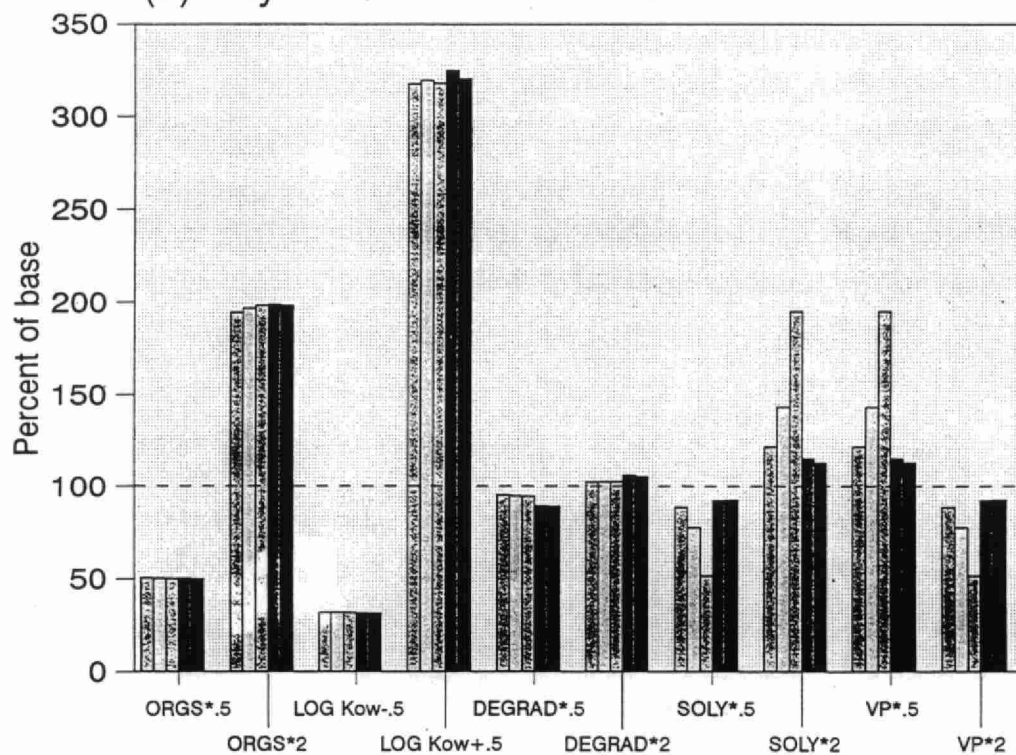
Figure 27: Sensitivity analysis for chloroform

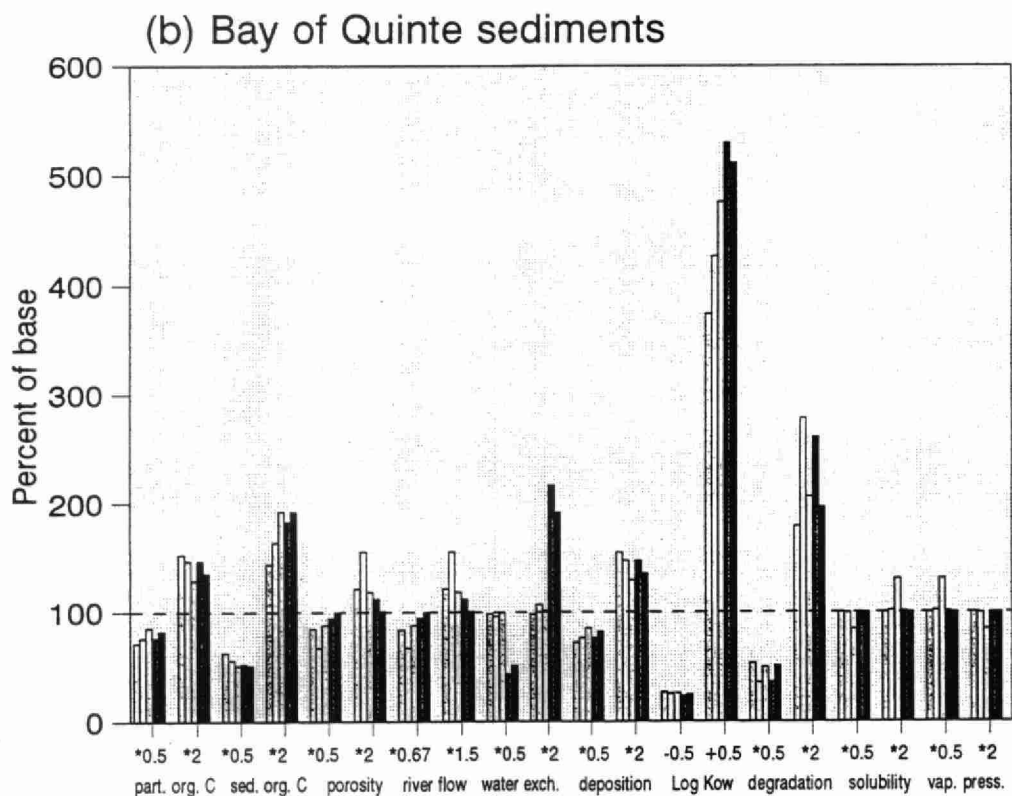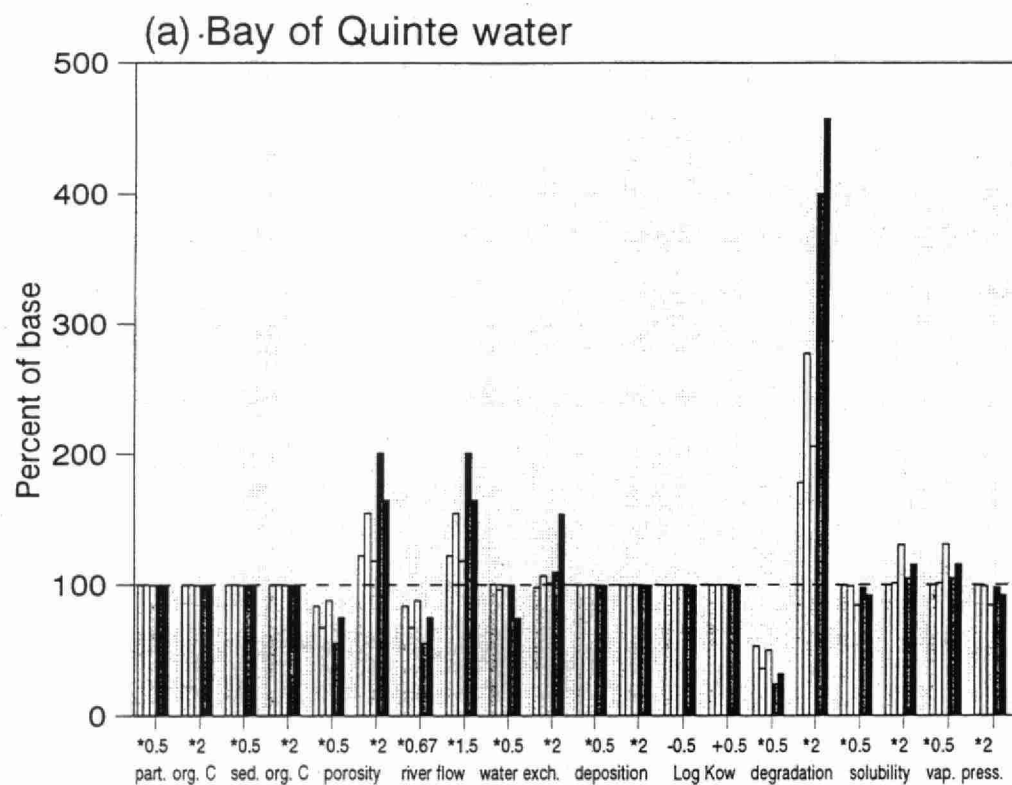## (a) Bay of Quinte water
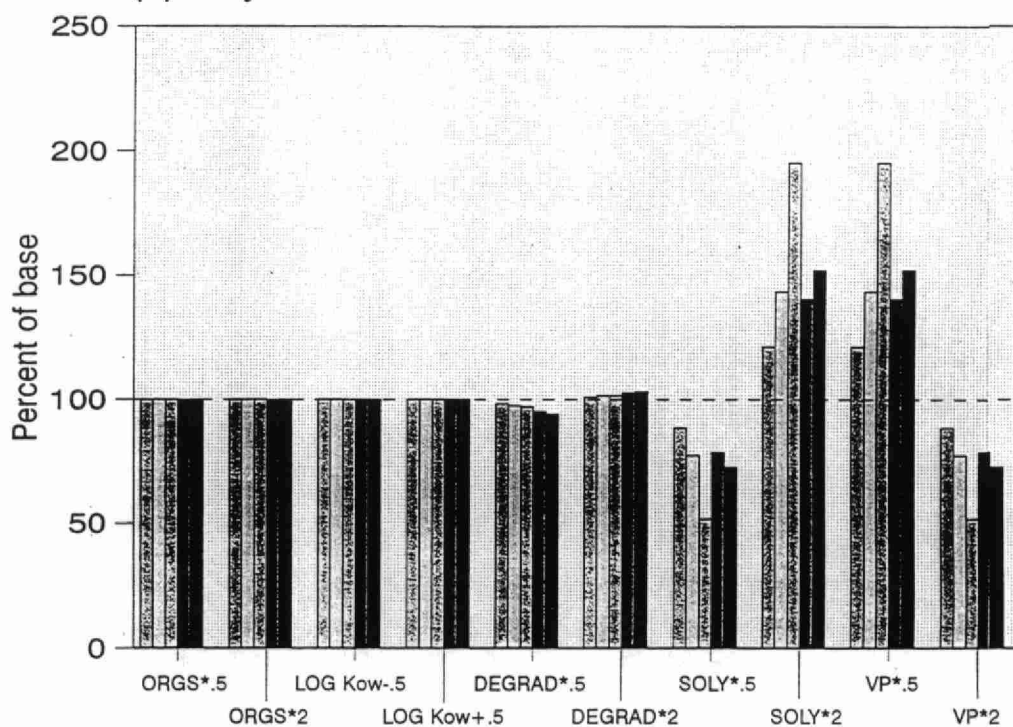
(b) Bay of Quinte sediments

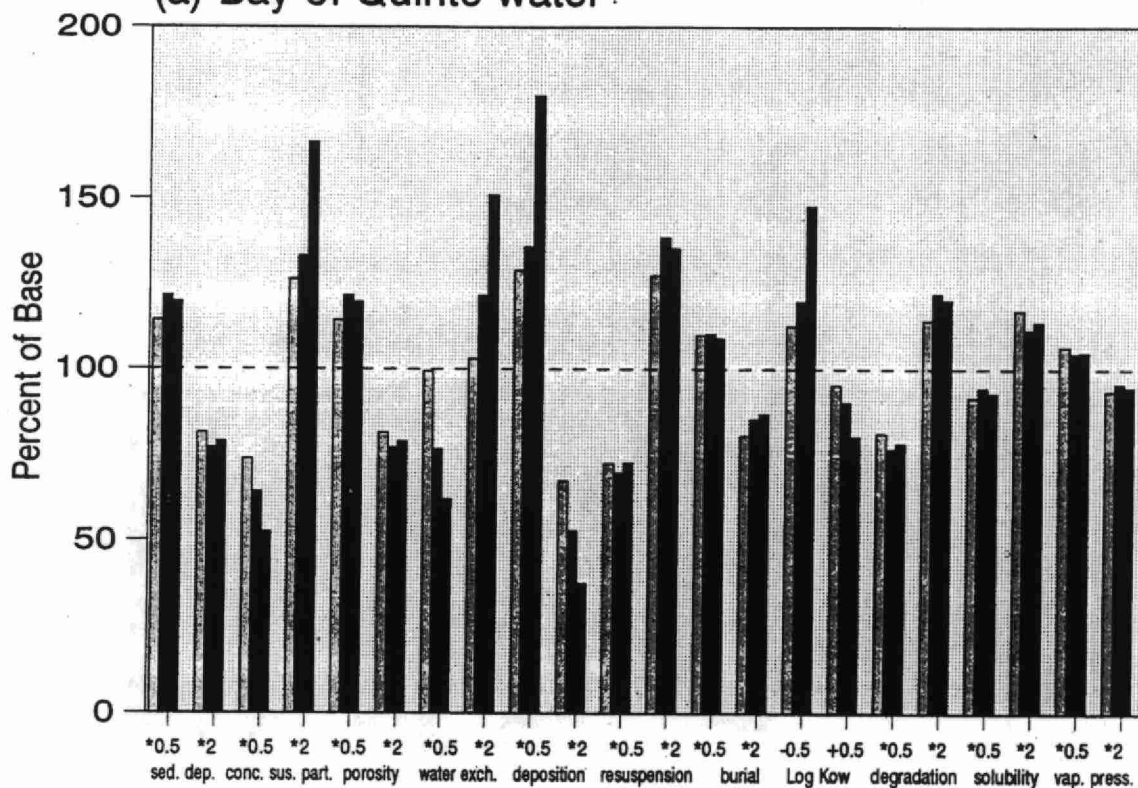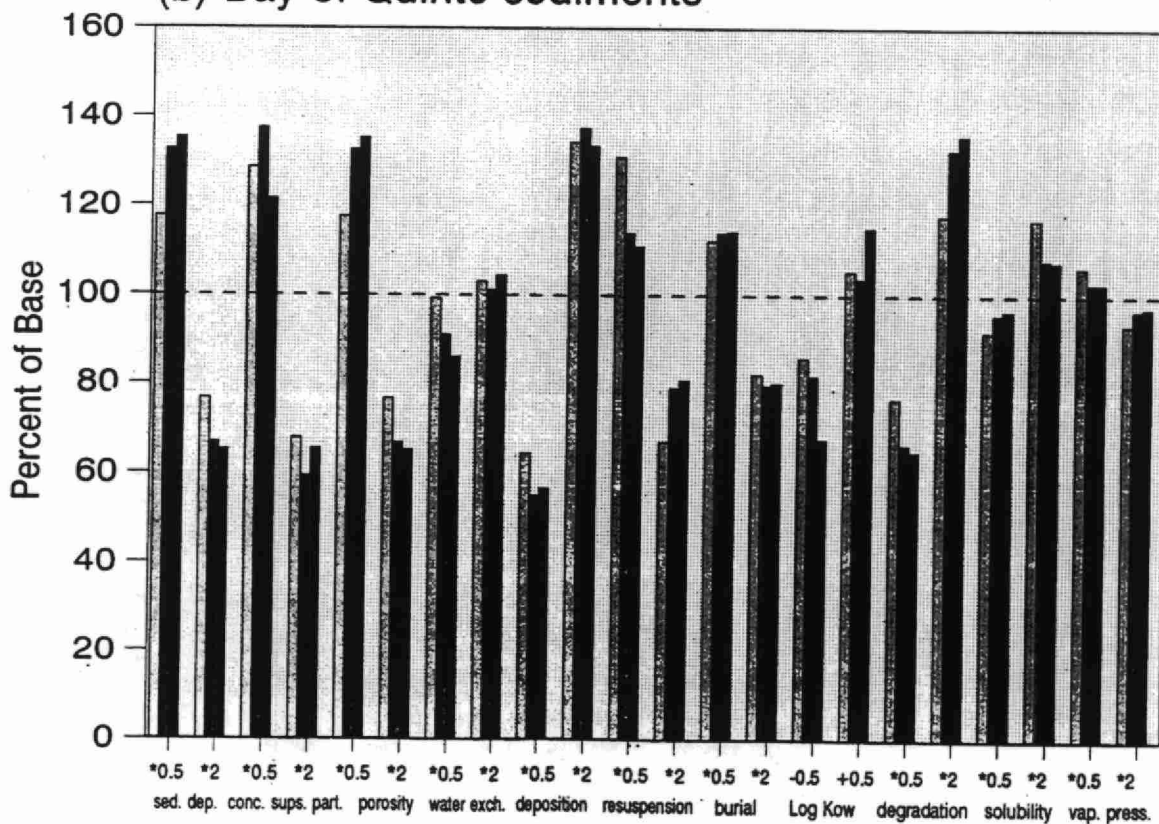Upper Bay W   Upper Bay E   Hay Bay   Middle Bay   Lower Bay

53

Figure 28: Sensitvity analysis for PCP

(a) Bay of Quinte water

(b) Bay of Quinte sediments

Upper Bay W   Upper Bay E   Hay Bay   Middle Bay   Lower Bay

Figure 29: Sensitivity analysis of 2,3,7,8-TCDD

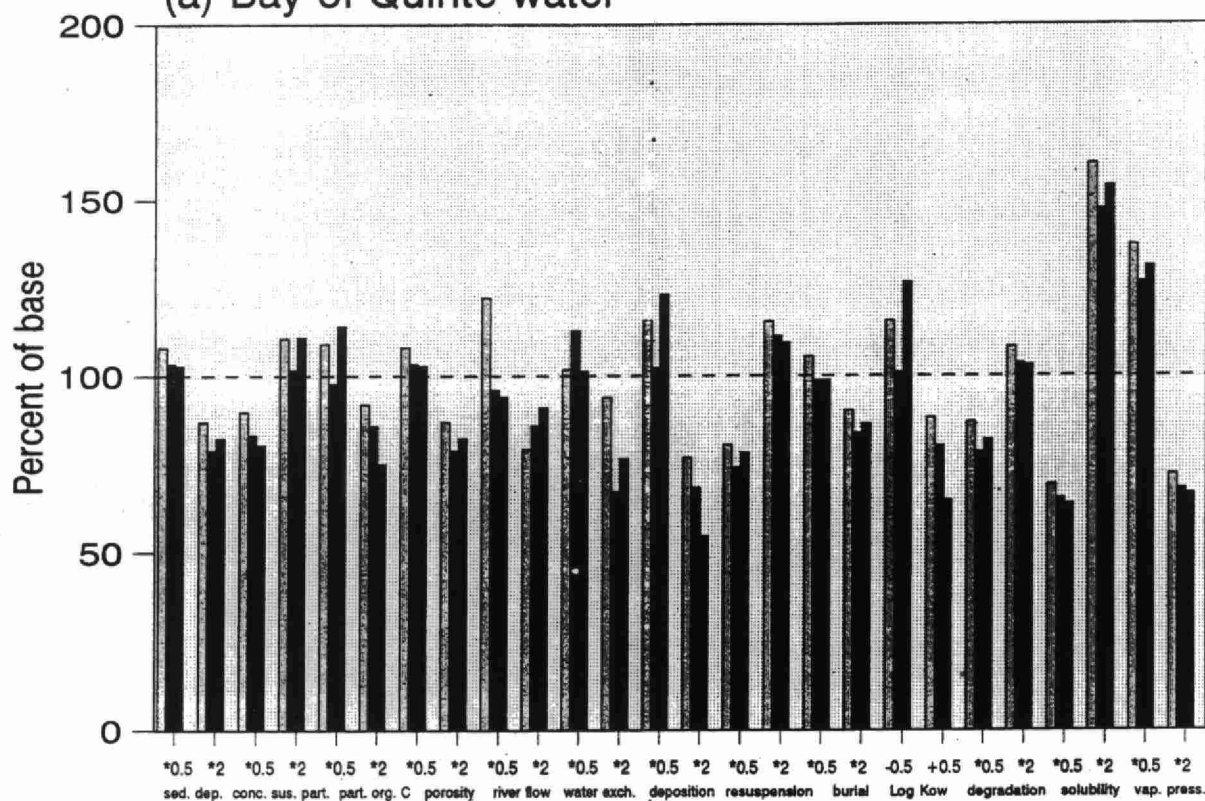## (a) Bay of Quinte water

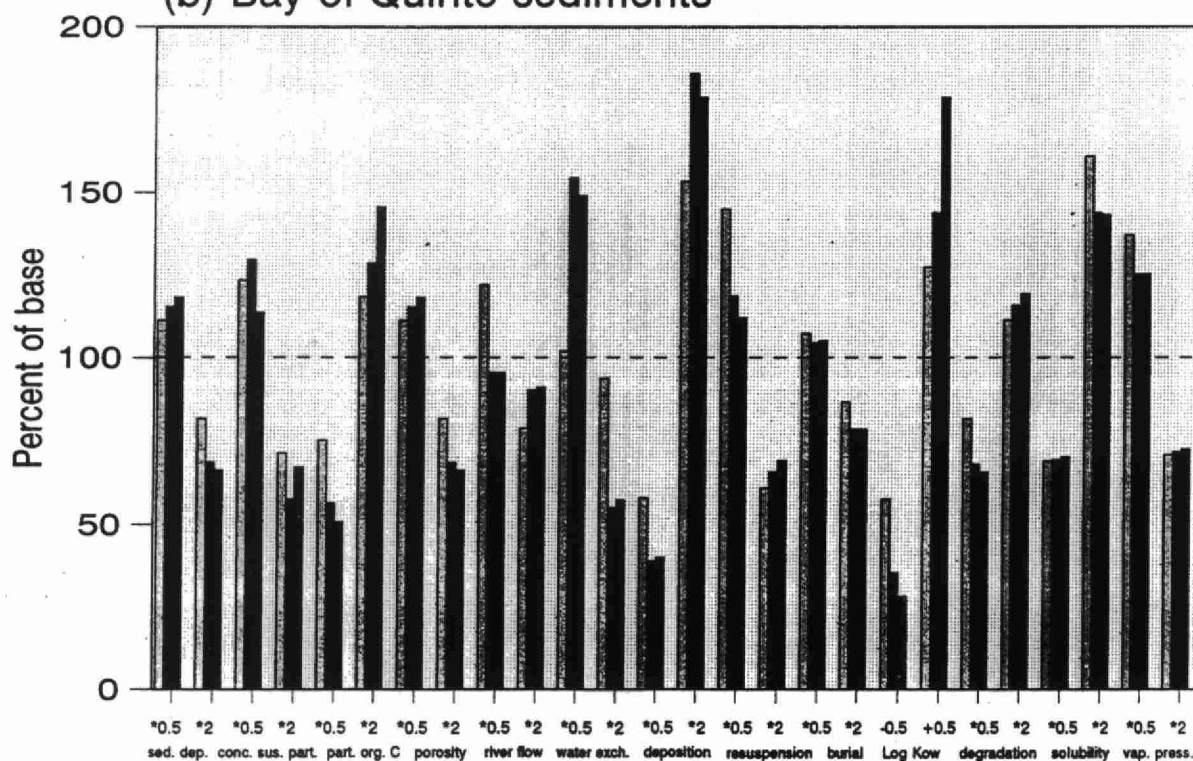## (b) Bay of Quinte sediments

☐ Upper Bay E   ▨ Middle Bay   ■ Lower Bay

55

Figure 30: Sensitivity analysis for 2,3,7,8-TCDF

(a) Bay of Quinte water

(b) Bay of Quinte sediments

☐ Upper Bay E ■ Middle Bay ■ Lower Bay
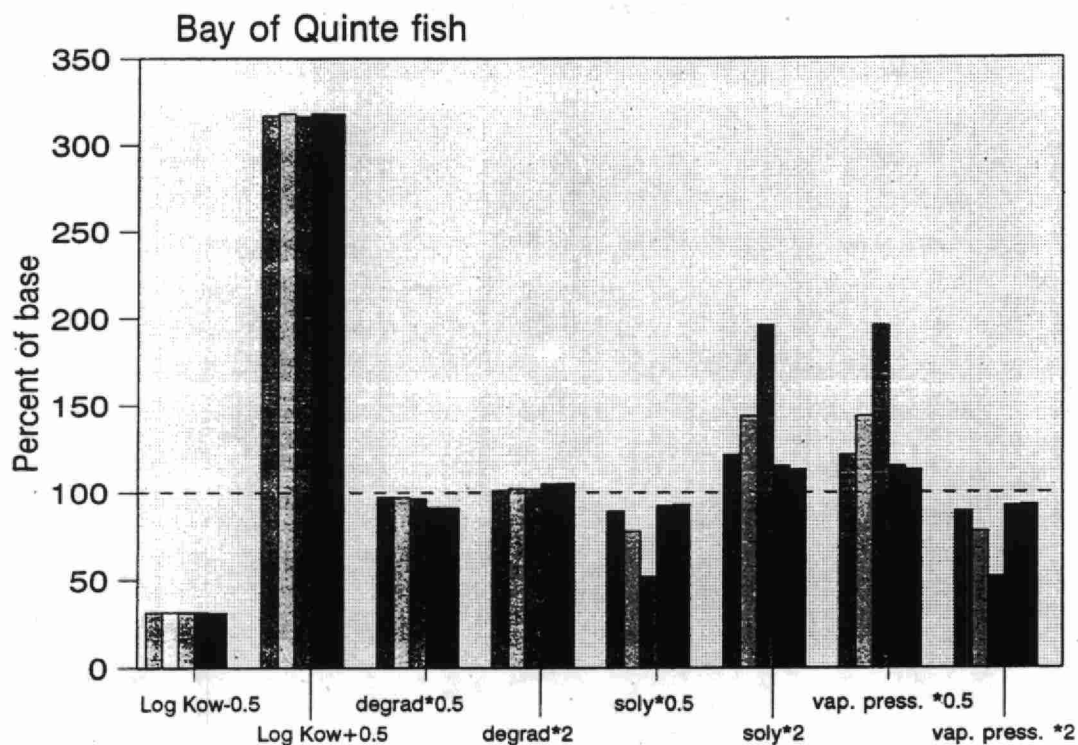
Figure 31(a): Sensitivity analysis for chloroform

Bay of Quinte fish
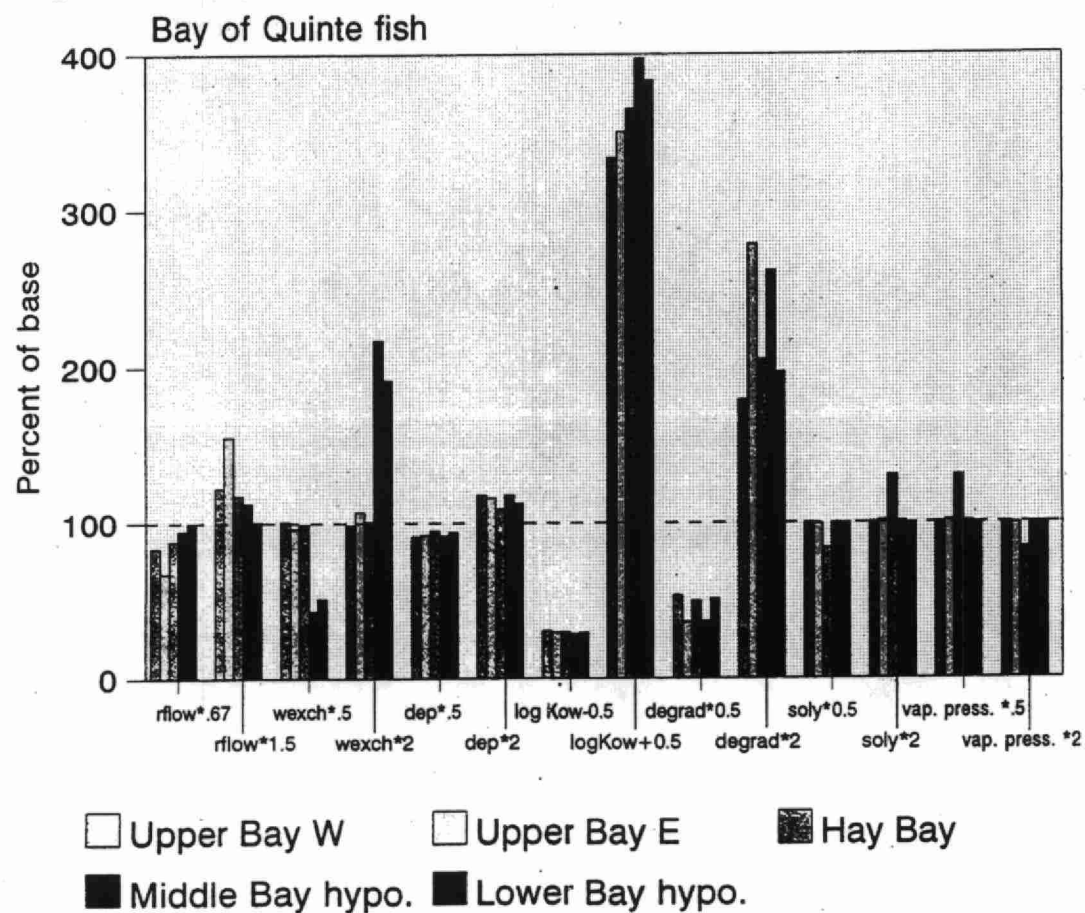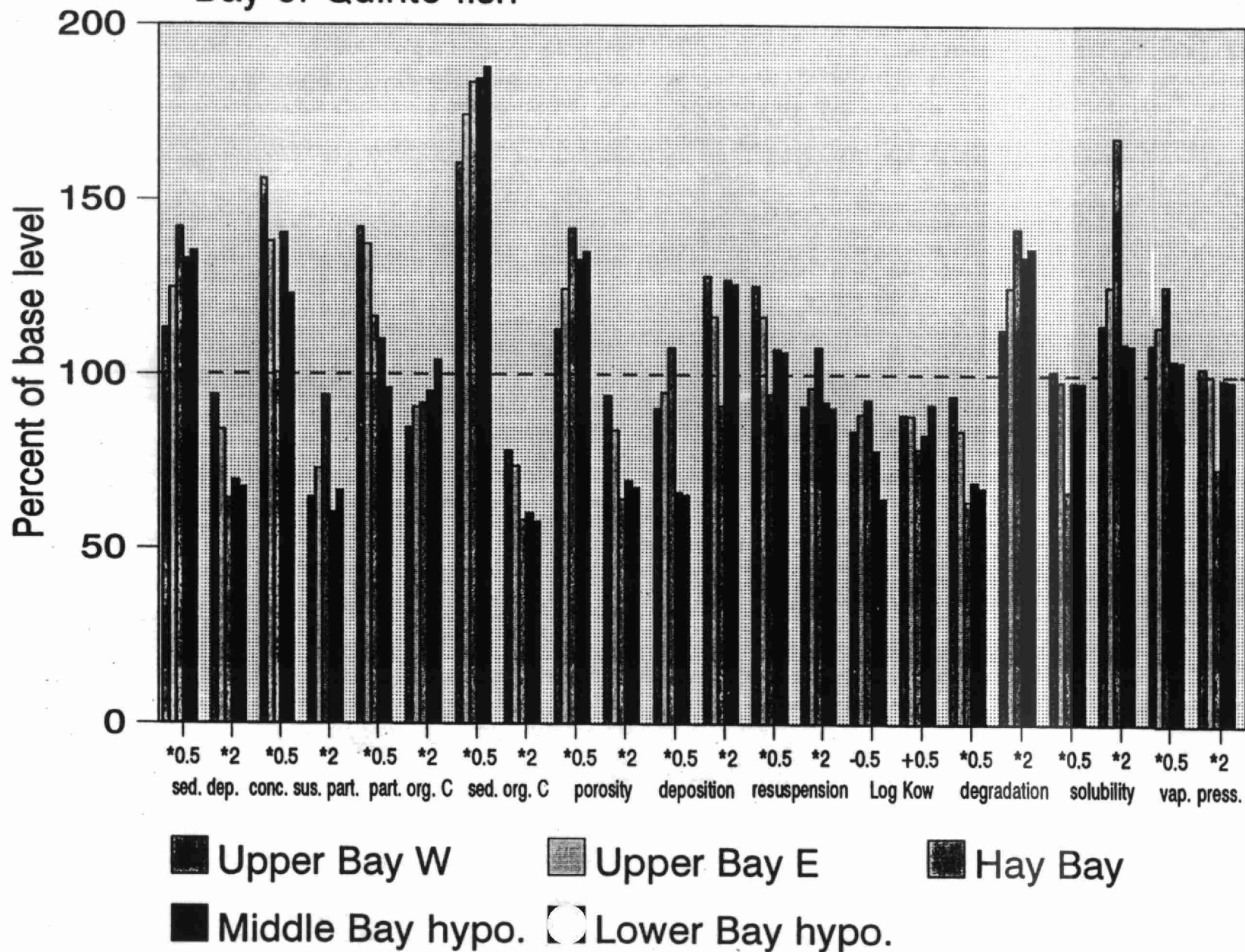

Figure 31(b): Sensitivity analysis for pentachlorophenol

Bay of Quinte fish

☐ Upper Bay W   ☐ Upper Bay E   ▨ Hay Bay

■ Middle Bay hypo.   ■ Lower Bay hypo.
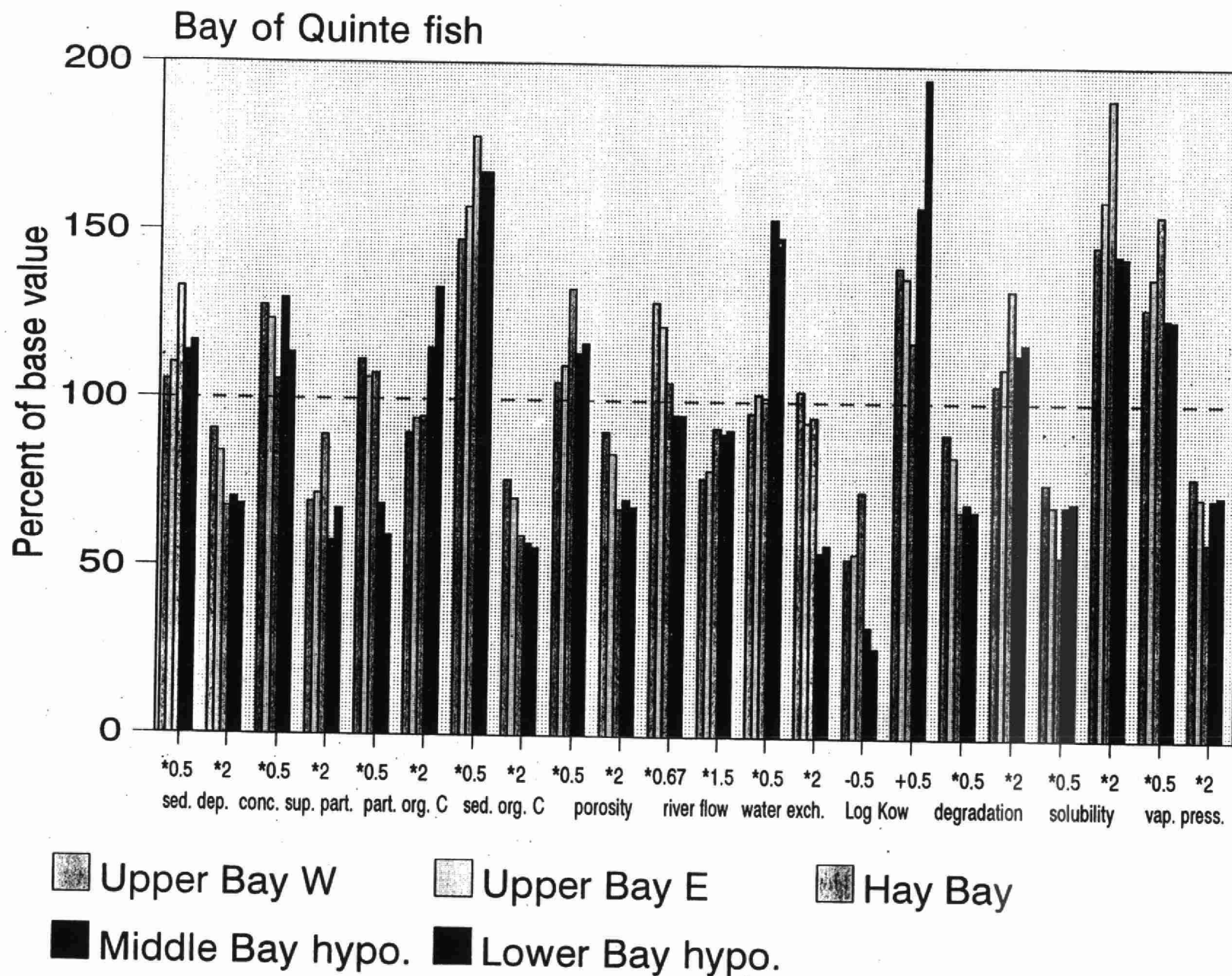
Figure 32: Sensitivity analysis for 2,3,7,8-TCDD
Bay of Quinte fish

Figure 33: Sensitivity analysis for 2,3,7,8-TCDF

Bay of Quinte fish

Percent of base value

200

150

100

50

0

*0.5 *2 *0.5 *2 *0.5 *2 *0.5 *2 *0.5 *2 *0.67 *1.5 *0.5 *2 -0.5 +0.5 *0.5 *2 *0.5 *2 *0.5 *2

sed. dep. conc. sup. part. part. org. C sed. org. C porosity river flow water exch. Log Kow degradation solubility vap. press.

Upper Bay W   Upper Bay E   Hay Bay

Middle Bay hypo.   Lower Bay hypo.

is quite sensitive to degradation rate, however, with the greatest effects (factor about 2.5) being found in Upper Bay East and Middle Bay hypolimnion. It is also sensitive (factor about 2) to water exchange in the Middle and Lower Bay hypolimnia.

TCDD and TCDF (Figures 32 and 33) again give a complex sensitivity pattern. The effects of sediment depth, concentration of suspended particles, degradation, solubility, vapor pressure, and (TCDF only) K_{ow} are similar to those with sediments. The effect of K_{ow} for both chemicals (especially TCDD) is much less than that for chloroform or PCP. Both chemicals are quite sensitive to sediment organic carbon, almost doubling for halved sediment organic carbon (SOC). Sensitivities are frequently quite different in different model segments. Again, it should be emphasized that these tests exclude the effect of food chain variables, which can play an important role in predicting the link between inputs of these chemicals and their biotic levels. In view of these significant model sensitivities and the low concentrations involved, it is hard to draw any conclusion about the effects of MISA-BATEA levels on fish (keeping in mind that the regulations state these substances should be "non-measurable at the available regulation method detection limit (RMDL)" (MOEE, 1993), and that one-tenth of RMDL values were used in loadings calculations. This in itself could easily result in an error of up to $\pm$ 100 percent in predictions.

5.3 Comparison of results to objectives and guidelines

All modelled chemical concentrations in water (see Table 7) are much lower than present PWQOs where defined (As, 100 μg/l; Cd, 0.2 μg/l; Cu, 5 μg/l; Pb, 25 μg/l (alk > 80 mg/L); Zn, 30 μg/l; PCP, 0.5 μg/l). PWQOs have not been defined for the other parameters. However, modelled metal concentrations in sediments (see Table 8) are generally above the new Provincial Sediment Quality Guidelines (PSQG) Lowest Effect Levels (LEL), and in a few cases (Cd and Pb in some segments), above the Severe Effect Levels (SEL). PSQG values are not available for the organic compounds, although interim values of 6.2 and 316 ng/g (ppt) have been calculated for 2,3,7,8-TCDD and 2,3,7,8-TCDF in Thunder Bay (R. Jaagumagi, pers. comm.) Predicted values for this compound at the input level of 10% of RMDL used are 2 x 10^{-3} to 3 x 10^{-2} ng/g and are hence well below the interim values.

The fact that modelled metal concentrations satisfy PWQOs but not PSWGs suggest there is some incompatibility between the two sets of objectives. Both sets of objectives are based on total concentrations of metals, although there is much evidence that chemical speciation of individual metals in both media controls their

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bioavailability and hence toxicity. In the sediments, much of the metals are bound in unavailable forms (e.g. aluminosilicate, adsorbed or complexed to natural organic matter, etc.). Although selective extraction methods (e.g. Tessier et al., 1979) may provide information as to relative bioavailability of metal forms, several authors have used simpler methods such as extraction with 1N HCl (e.g. Krantzberg, 1992; Luoma, 1983) and found significant correlations with metal tissue levels in deposit-feeding clams (*Scrobicularia plana*) (Luoma, 1983). Correlations were improved when the ratio of 1N HCl-extracted Pb to 1N HCl-extracted Fe was used as a predictor of Pb levels in the same organism (Luoma and Bryan, 1978). Results of the modelling study strongly suggest a need for reformulation of sediment guidelines as a function of some operationally-defined bioavailable metal fraction.

In water, the free metal ion is the most toxic form for most metals; toxicity is much reduced for metals complexed to ligands such as carbonate, chloride, natural dissolved organic matter, etc. A metals equilibrium model, MINTEQA2 (Allison et al., 1991), can be used to predict free metal ion concentrations. Work is underway to apply this model to test Great Lakes systems.

Very little information exists for sport fish guidelines for the organic chemicals monitored (A. Hayton, pers. comm.) There is no sport fish guideline for chloroform. If a guideline existed for PCP, it would be between 6 - 12 μg/g. Any experimental data available are below the detection limit of 50-100 ng/g; the predicted values (Figure 14) are of the order of 0.4 - 1.4 ng/g. For TCDD and TCDF, the guideline is 0.015 ng/g (ppb) total toxic equivalents of all dioxin and furan congeners. Data of Figures 18 and 20 suggest a possible exceedence of this guideline; however, these results were based upon an interpretation of "no measurable input" of dioxins and furans as meaning 0.1*RMDL (see data on inputs, section 3.0). Considering the large uncertainties in modelling of these compounds (see also section 5.2) and the fact that MOEE data in 1989 (cited by Poulton, 1990), no comparisons with guidelines for these compounds are possible.

5.4   Effect of atmospheric contaminant levels on model results

As atmospheric inputs (section 3.0; Reid et al., 1993; MOEE, 1994) showed a considerable variability and in some cases were observed to be considerably higher than assumed data used by Diamond et al. (1992), a separate sensitivity analysis was done on the value of this input. The base result was compared with results obtained by doubling the input, halving it, and eliminating it entirely. Results are given in

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Figures 34-35 for inorganics and Figures 36-38 for organics in water, sediment and fish. In each of these figures, each block of bars represents results for one chemical as indicated beneath; data are given only for three model segments, for simplicity.

The shallow Hay Bay segment is most affected by variations in atmospheric input of all chemicals. This is especially true for organics where there is little or no other input to this segment, except for intersegment exchange. Hence, disagreement between modelled and observed results found for some chemicals could at least partially originate from this source. The relative effect of changing atmospheric input is very similar in all three media with both inorganic and organic chemicals for a given segment and chemical. This reflects the equilibrium (fugacity/aquivalence) nature of the model. Some exception to this does occur in the Lower Bay due to the amount of chemical exchanged with Lake Ontario.
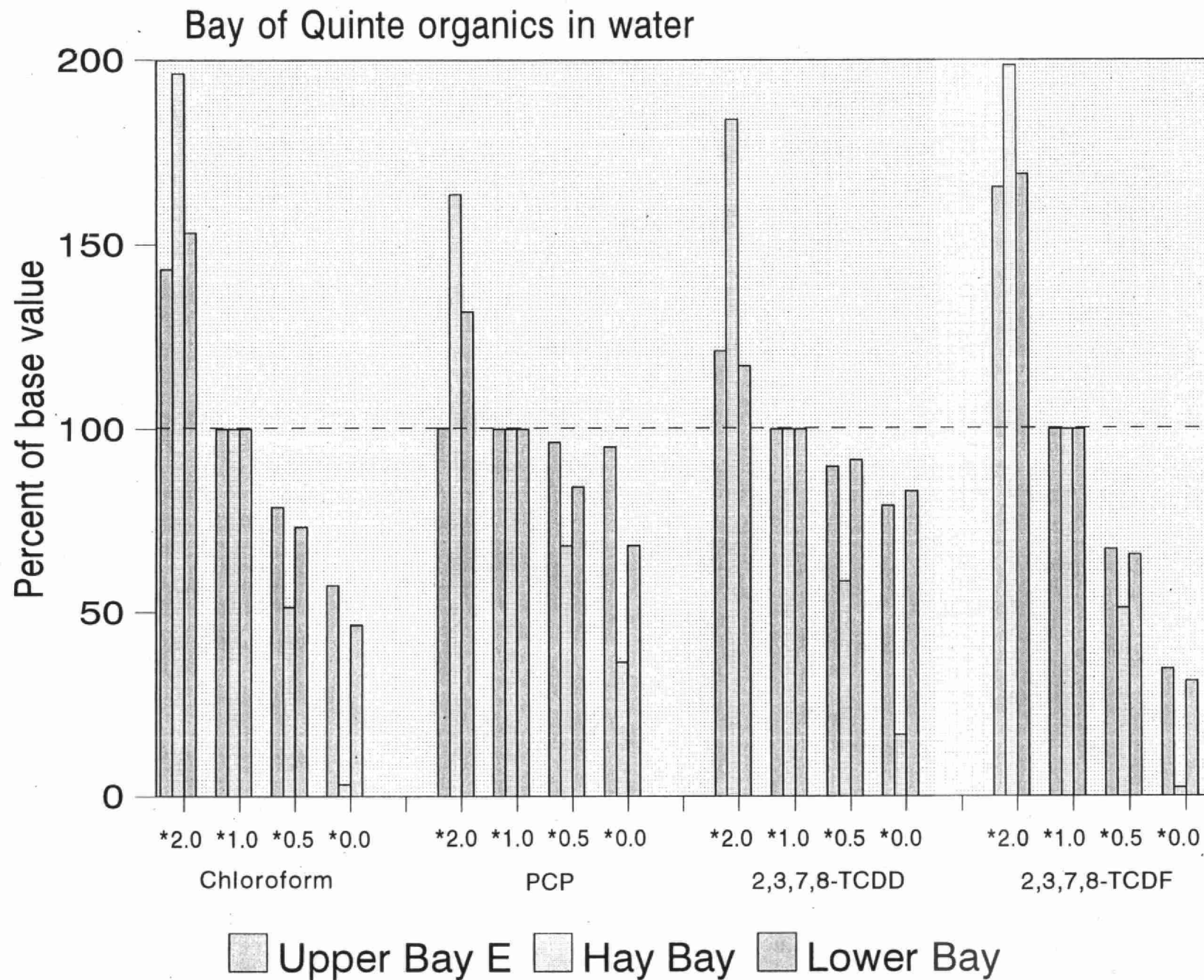
Figure 34: Effect of varying atmospheric input

Bay of Quinte inorganics in water

Upper Bay E ☐ Hay Bay ☐ Lower Bay
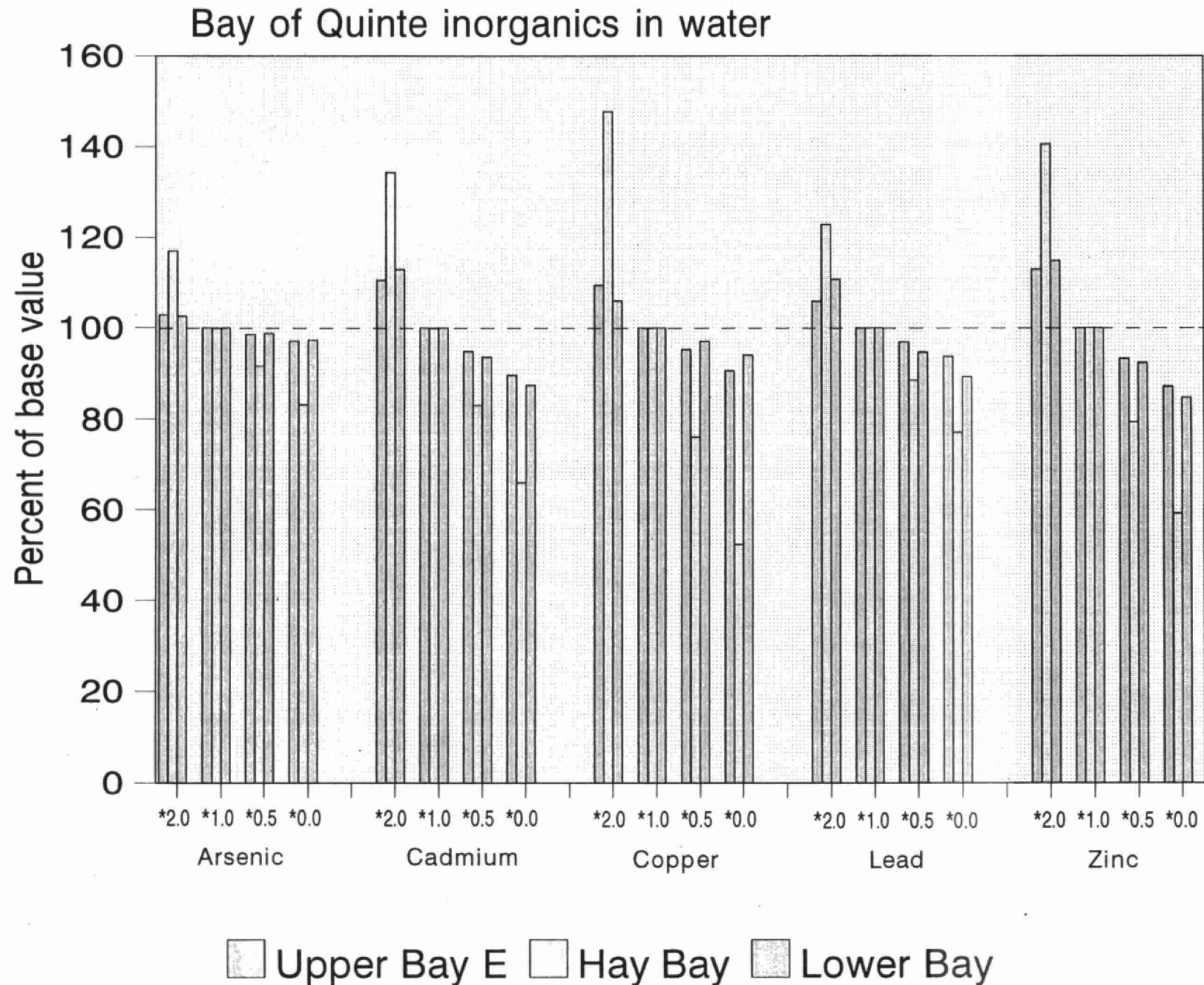
Figure 35: Effect of varying atmospheric input

Bay of Quinte inorganics in sediment
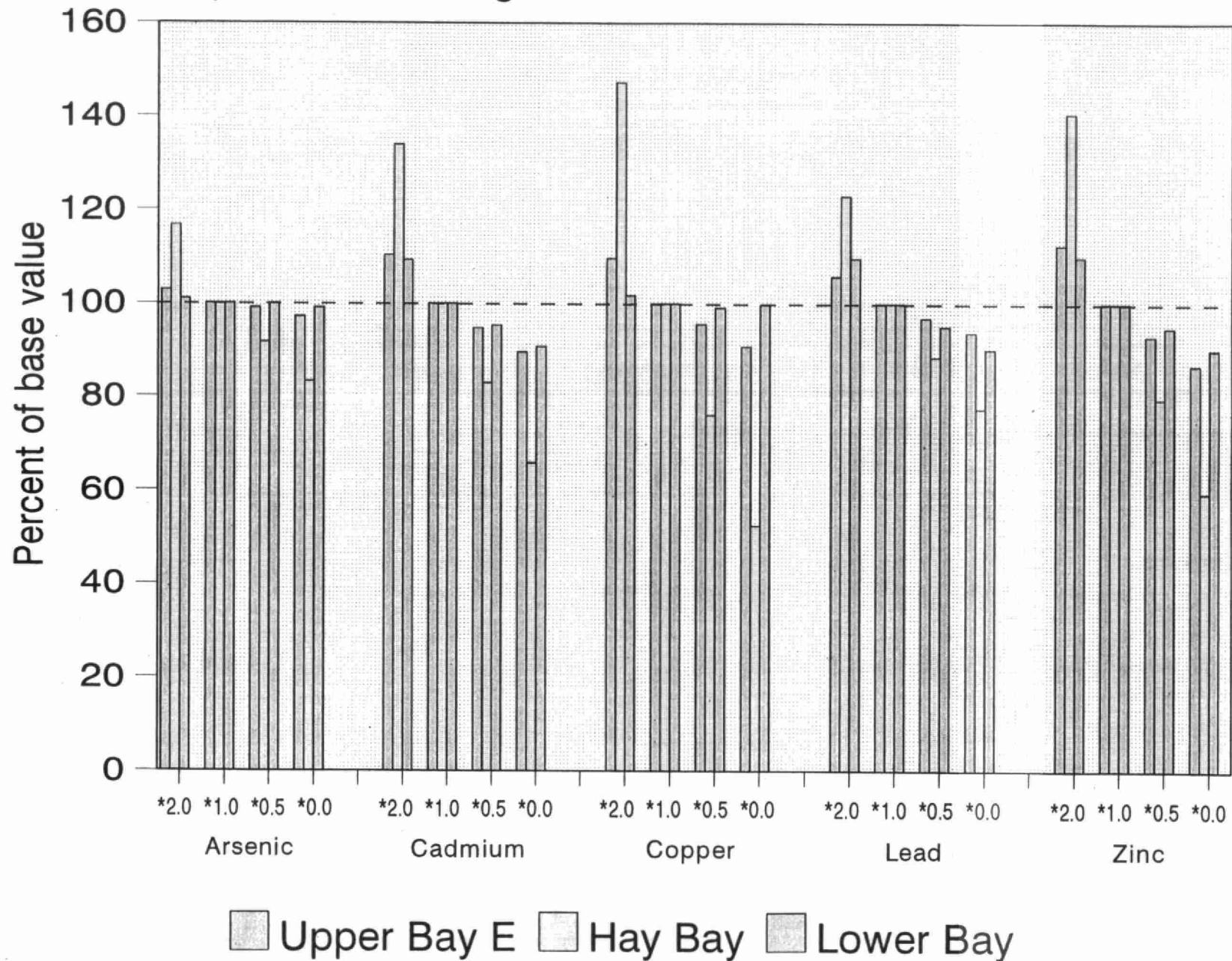
Figure 36: Effect of varying atmospheric input

Bay of Quinte organics in water

65

Upper Bay E ☐ Hay Bay ☐ Lower Bay

Figure 37: Effect of varying atmospheric input

Bay of Quinte organics in sediment
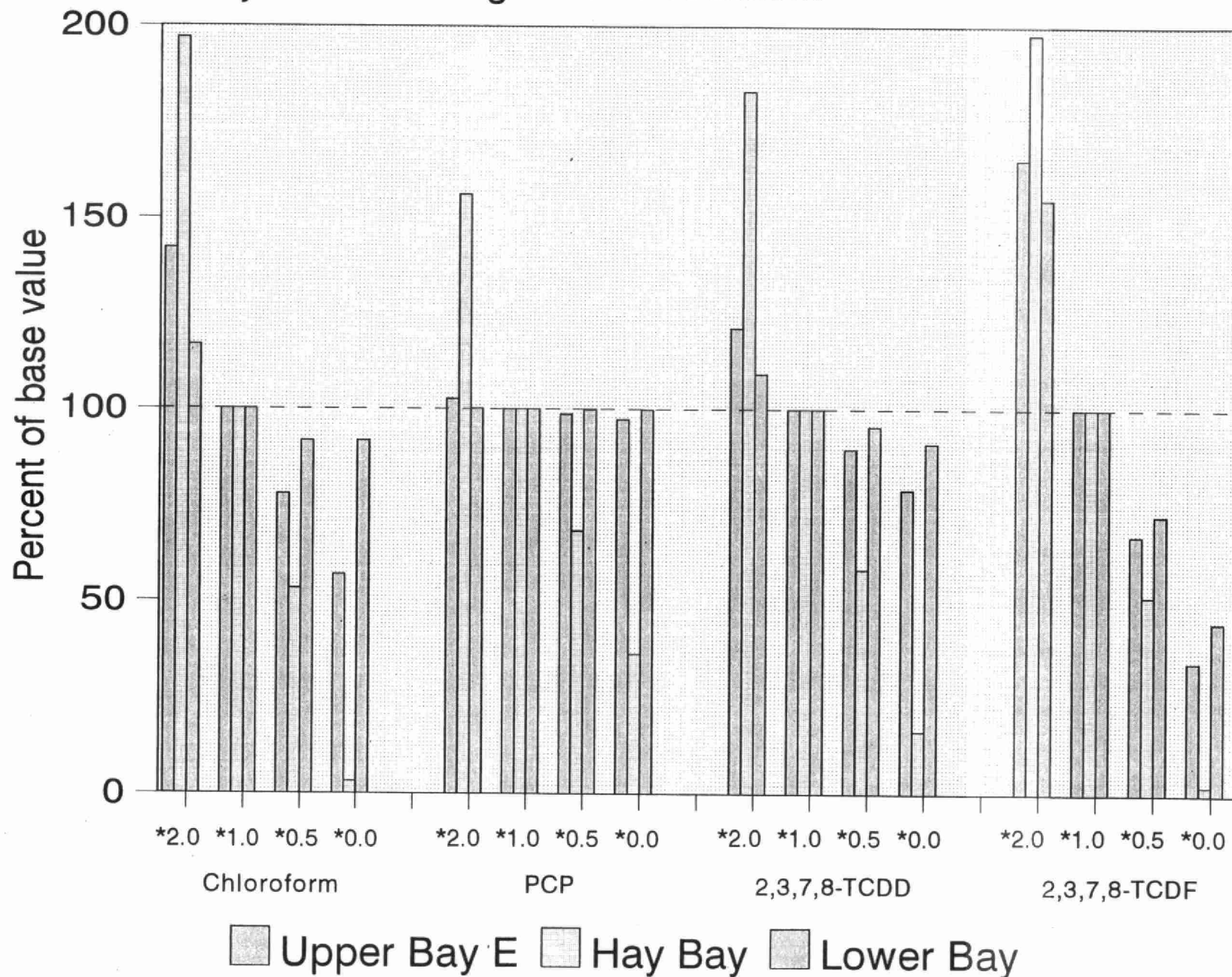
Figure 38: Effect of varying atmospheric input

Bay of Quinte organics in fish

Upper Bay E   Hay Bay   Lower Bay
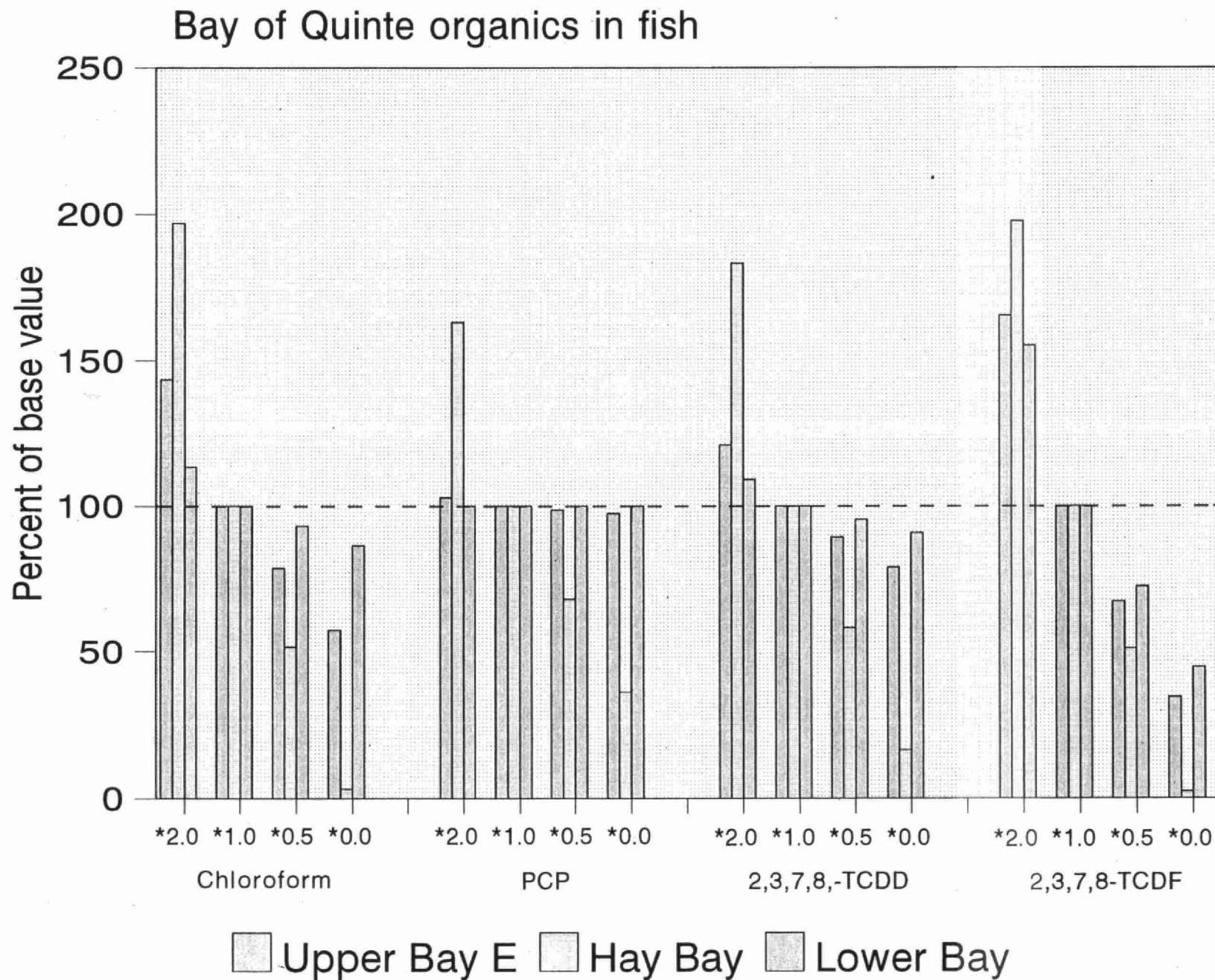
6.0   CONCLUSIONS

This report has updated earlier model results for the Bay of Quinte Area of Concern using the most recent available input data as well as the MISA-BATEA effluent limit regulations for chloroform, TCDD and TCDF in the pulp and paper sector. The sensitivity of model predictions to input parameters and atmospheric loadings has also been examined. Some specific conclusions follow:

1.   Predicted concentrations of all chemicals examined in water are within the Provincial Water Quality Objectives. However, predicted sediment metal concentrations continue to exceed the Provincial Sediment Quality Guidelines. This suggests a disparity in the two sets of guidelines which may be related to the effect of chemical speciation on toxicity tests used to establish the objectives. Predicted levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF are below the interim calculated values for Thunder Bay (R. Jaggumagi, pers. comm.).

2.   Predicted concentrations of organic chemicals in fish are within guidelines for pentachlorophenol. It is difficult to assess guidelines for TCDD and TCDF, as they are expressed as toxicity equivalents for all congeners together; the modelling of congeners other than the 2,3,7,8-tetrachloro congeners was beyond the scope of this study. In addition, the MISA-BATEA regulation depends upon the regulation detection limit (RMDL), which appears to be too high to accurately define fish levels.

3.   Predicted concentrations of arsenic, copper, zinc and pentachlorophenol are significantly lower than those of Diamond et al. (1992), as a result of reductions in point source and tributary input. This report contains the first predictions of lead concentrations in the Bay. Modelled lead concentrations in water are similar to observed (1988) values; however, modelled sediment lead concentrations are considerably higher than observed, possibly due to the value of partition coefficients used.

4.   Updated information for atmospheric concentrations of certain chemicals, especially cadmium, have resulted in predicted concentrations higher than those of Diamond et al. (1992), despite reported decreases in point source and tributary loadings. It is felt that the more recent results should more accurately reflect actual conditions; however, sensitivity analyses based on atmospheric

inputs suggest that predictions in shallow Hay Bay can be strongly influenced by atmospheric inputs.

5.   Model results for cadmium, chloroform, TCDD, and TCDF are only approximate due to the presence of a large number of "non-detects" in the input data. This is particularly true for TCDD and TCDF. In addition, the values obtained for the latter two chemicals are very sensitive to the physical parameters in the model, and could conceivably be calibrated to a large number of different sets of physical parameters. Especially for TCDD and TCDF, the predictions are only crude order of magnitude estimates.

6.   Model results for metals, chloroform and PCP in water are insensitive to the values of most physical parameters. River flow, concentration of suspended particulates, sediment resuspension and burial are the most sensitive parameters for most metals. Chloroform is sensitive to solubility and vapor pressure, while PCP is sensitive to degradation rate. In sediments, deposition, resuspension and burial from the active layer tend to be important for most metals, while K_{ow} and sediment organic C are important for organics. As mentioned above, modelled values of TCDD and TCDF are quite sensitive to a large number of physical parameters.

7.0   Recommendations

The major purpose of this study was to determine the effect of MISA-BATEA discharge regulations, where available, and updated measured data on Bay of Quinte water and sediment quality, and its compliance with objectives and guidelines. While water concentrations generally meet objectives, sediment concentrations still exceed the new Provincial Sediment Quality Guidelines. As the model is based upon equilibrium conditions, this suggests a disparity between the two sets of objectives.

It is recommended that:

1.   Additional work be undertaken with regard to measuring low-level concentrations of both metals and organics in Bay of Quinte water. This should include not only the chemicals modelled in this study, but other substances of concern such as PCBs, chlorinated pesticides, lower chlorinated phenols and agricultural chemicals such as atrazine.

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2. Levels of bioavailable metals and organics in water and sediments should be measured (e.g. by use of a sediment extractant such as 1N HCl). Bioavailability of metals can be assessed using an equilibrium speciation model such as MINTEQA2, and relating the results obtained to toxicity studies in effluents.

3. Objectives for contaminants in water and sediment should be refined so as to be compatible with each other in an equilibrium system as defined by suitable models, including the Mackay-Diamond model used here, and MINTEQA2.

4. Model results should be reevaluated as further MISA-BATEA discharge regulations are approved, and the results used to continually reassess the need for further remediation.

5. Efforts to clean up the arsenic-contaminated abandoned mine wastes at DeLoro should be continued.

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Remedial Action Plan
Plan d'Assainissement

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Canada-Ontario Agreement Respecting Great Lakes Water Quality
L'Accord Canada-Ontario relatif à la qualité de l'eau dans les Grand Lacs